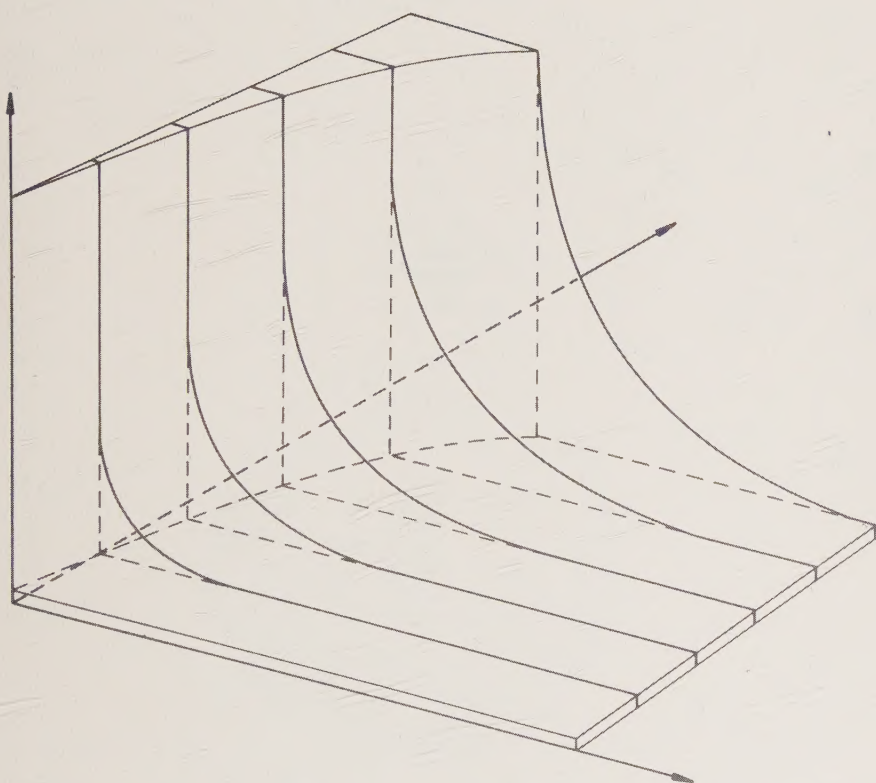
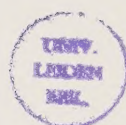


MACROMOLECULAR ADSORPTION AND FOULING IN ULTRAFILTRATION AND THEIR RELATIONSHIPS TO CONCENTRATION POLARIZATION

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May 1984
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AND THEIR RELATIONSHIPS TO CONCENTRATION POLARIZATION

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Center, Lund University, Alnarp, Sweden.

This thesis consists of this summary and of the following
papers, which will be referred to by their Roman numerals

I Concentration Polarization and Fouling.

E. Matthiasson and B. Sivik

Desalination, 35 (1980) 59-103.

II Solute Adsorption as a Source of Fouling in Ultra-
filtration.

M. López-Leiva and E. Matthiasson

Proc. from the International Workshop on the Funda-
mentals and Applications of Surface Phenomena Asso-
ciated with Fouling and Cleaning in Food Processing,
Tylösand, Sweden, 1981, pp 299-308.

III The Role of Macromolecular Adsorption in Fouling of
Ultrafiltration Membranes.

E. Matthiasson

Journal of Membrane Science, 16 (1983) 23-36.

IV Adsorption Phenomena in Fouling UF-Membranes.

E. Matthiasson, B. Hallström and B. Sivik

Engineering and Food, Vol 1, Proc. from the Third
International Congress on Engineering and Food,
Dublin, Ireland, September 1983.

V Predictions of Concentration Profiles in an Un-
stirred Ultrafiltration Batch Cell.

E. Matthiasson

Submitted for publication to J. Membrane Science

SUMMARY

The principal objective of this work has been to study the role of macromolecular adsorption in the fouling of ultra-filtration membranes.

Reduction in permeability of membranes made out of cellulose acetate, polysulfone and polyamide after being exposed to solutions of bovine serum albumin (BSA) has been measured and the amount BSA adsorbed estimated by using ^{14}C labelled proteins.

The properties of the protein solution had a large effect on the adsorption process. With increasing concentration increasing adsorption was found in the whole solubility range of the BSA proteins.

The flux resistance of the adsorbed layer was found to vary with the protein concentration during adsorption. The first protein layer, formed when the membrane was exposed to 0.4 g/100 ml BSA concentration, presented the highest specific resistance. On top of this dense layer a protein layer of very low resistance was formed but as the solute concentration became closer to the solubility limit of the BSA proteins the specific resistance increased gradually.

A derivation for the reduction in flux caused by adsorption as a function of concentration is presented. An equation giving the permeate flux as a function of the reduction in flux due to adsorption and the osmotic pressure of the solution is also presented.

The pH of the protein solution had a large influence on the adsorption process. The hydrophobic polysulfone and polyamide membranes had a maximum in adsorption at pH 4.7 (I.E.P. of BSA) while the cellulose acetate membrane presented a continuous increase in adsorption when going from pH 7 to pH 3.

Increasing ionic strength of the solution decreased the reduction in flux due to adsorption of BSA especially at high concentrations.

The adsorption kinetics of BSA on the membrane surface were found to be primarily diffusion controlled.

Numerical calculations of the concentration profiles of BSA in an unstirred batch cell showed that the wall concentration is highly dependent on the diffusion coefficient. Prediction of the permeate fluxes with the equation described above gave reasonable good agreement for diffusion coefficient of BSA equal to $6.2 \times 10^{-11} \text{ m}^2/\text{s}$ and the osmotic pressure expression found in the literature.

Comparison of the calculated wall concentration with the experimental flux data showed that some secondary hydraulic resistance existed in the unstirred batch cell ultrafiltration in addition to the resistances of the membrane and the adsorbed layer.



CONTENTS

1.	INTRODUCTION	1
2.	PROPERTIES OF BOVINE SERUM ALBUMIN	2
3.	MACROMOLECULAR ADSORPTION ON SOLID SURFACES	4
4.	STUDIES OF ADSORPTION FOULING IN UF	8
5.	ADSORPTION STUDIES	11
5.1	Introduction	11
5.2	Experimental	12
5.2.1	Materials	12
5.2.2	Hydraulic resistance measurements ...	13
5.2.3	Labelling of BSA	14
5.3	Concentration dependency of the adsorption .	16
5.3.1	Adsorption at low concentration	18
5.3.2	Adsorption at high concentration	21
5.4	Influence of air on the adsorption	23
5.5	pH dependency	25
5.6	Ionic strength of the solution	27
5.7	Adsorption kinetics	29
5.8	The hydraulic resistance of the adsorbed layer	29
6.	ULTRAFILTRATION IN AN UNSTIRRED BATCH CELL	32
6.1	Prediction of concentration profiles	32
6.2	Secondary hydraulic resistance layer	33
6.3	Prediction of permeate fluxes	34
7.	CONCLUSIONS AND FUTURE ASPECTS	35
8.	ACKNOWLEDGEMENTS	39
9.	REFERENCES	40

1. INTRODUCTION

Fouling in ultrafiltration of macromolecular solutions is a phenomenon that has been studied quite frequently during the last two decades. The models developed to predict the transmembrane flux in ultrafiltration take into account some of the physical properties and other characteristics of the macro-solute.

The properties of the macromolecular solutions which are most often considered are the ability to form a gel when the solubility limit is reached, the concentration dependent diffusivity and the osmotic pressure.

In spite of the fact that the models most often give a good qualitative description of the flux behaviour in ultrafiltration, deviations are frequently observed in experiments. This gives a clear indication that the theories do not give a full description of the fouling phenomenon and that there are some factors which are of major importance and which are not included in the models.

It is well known that macromolecules like proteins interact with almost all interfaces. This property is of great biological importance in nature. There is reason to believe that this characteristic of proteins and other macromolecules can be of importance in ultrafiltration and affect both the separation ability and the hydraulic resistance of the membrane. In the ultrafiltration literature there are a number of experimental facts attributed to adsorption of macromolecules. Most often no direct evidence is sought for these statements nor any further investigation performed in order to obtain better knowledge of the importance of this phenomenon.

The main objective of the work presented in this thesis is to study the role of macromolecular adsorption in the fouling of ultrafiltration membranes. The influence of the solution properties as well as the membrane characteristics on the adsorption of bovine serum albumin (BSA) and the effect they produce

on the membrane performance has been studied. The importance of this adsorption process in relation to the resistance of the membrane and the concentration polarization layer in an ultrafiltration process has also been investigated.

2. PROPERTIES OF BOVINE SERUM ALBUMIN

Bovine serum albumin (BSA) proteins are frequently used in ultrafiltration experiments especially when studying fundamental principles of the process and the surface fouling.

Its molecular weight is reported to be $66\,700 \pm 400$ dalton (1) but values in the range $66\,000 - 69\,000$ dalton are often given in the literature mainly due to the fact that the samples contain some amount of dimers and higher polymers. The shape of hydrated BSA monomer is ellipsoid with the major axis of $140\text{ \AA}$ and the minor axis $40\text{ \AA}$ (1). Through the work of J.R. Brown et al (2) the amino acid sequence of BSA is known (Fig. 1).

The isoelectric point is close to pH 4.7. The solubility limit at pH 7 is about 58 g/100 ml (3) while at pH 4.7 it is around 34 g/100 ml (4).

The dynamic viscosity of the BSA solution as a function of concentration (5) at pH 6.7 is given by the empirical equation $\mu = \exp(2.44 \times 10^{-3} \cdot c^2)$ where μ is in CP and c is the concentration in g/100 ml. This expression is valid up to 45% concentration. The viscosity was found to show negligible dependency on the pH and type of buffer solution.

The diffusion coefficient in dilute solutions is reported to be in the range $5 - 7.5 \times 10^{-11} \text{ m}^2/\text{s}$ at pH 7 (4). Diffusivity data at high concentration is limited and inconsistent (see paper V).

This also accounts for the osmotic pressure of the BSA solution. The measurements of Scatchard et al (6) and Vilker et al (7) differ a lot at pH 7 for concentrations above 12 g/100 ml (see paper V).

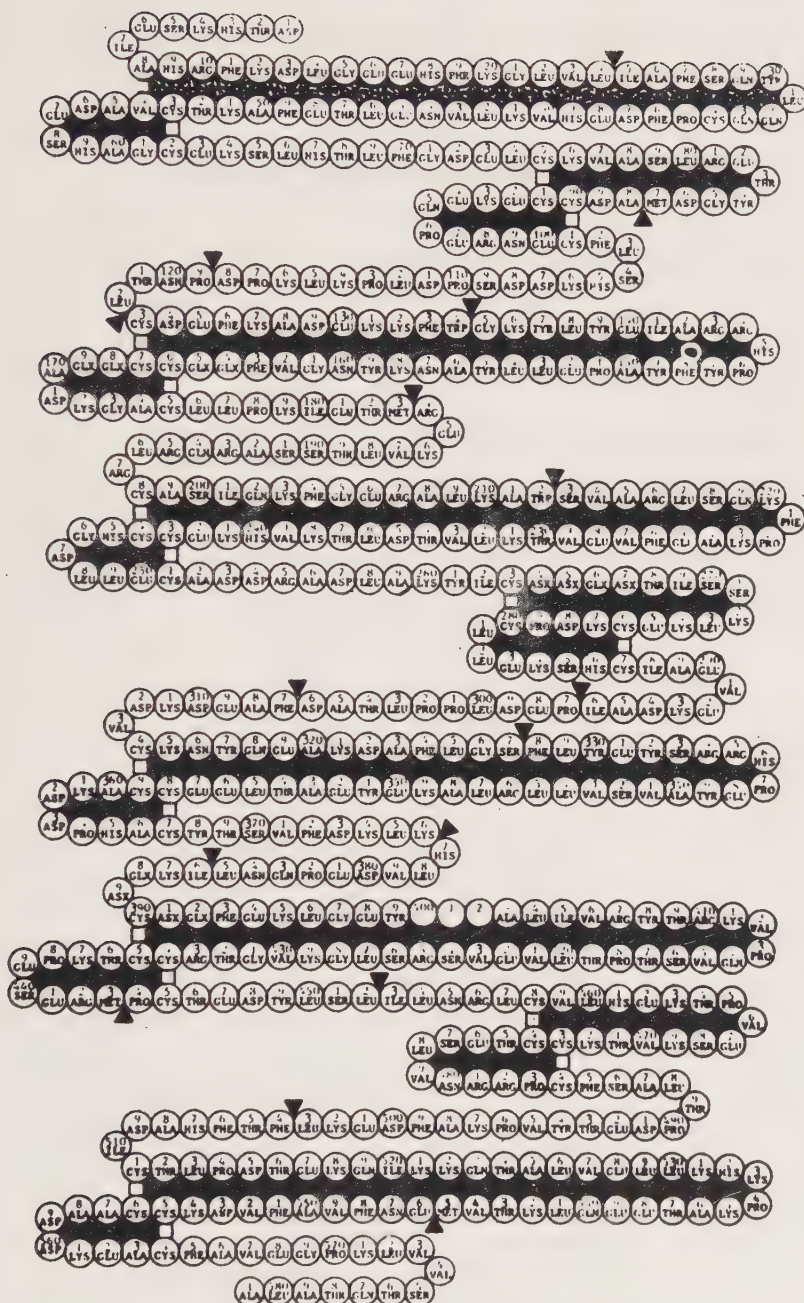


Fig. 1. The amino acid sequence of BSA (J.R. Brown Fed. Proc. 34, 1975, p. 591).

The density of BSA solutions 0.15 M NaCl at pH 7.0 as a function of concentration was found in paper V to be represented by the equation

$$\rho = 2.53 c + 1\ 000$$

where ρ is the density in kg/m^3 and c the concentration of BSA in g/100 ml.

3. MACROMOLECULAR ADSORPTION ON SOLID SURFACES

The adsorption of macromolecules at interfaces has become a very interesting field of research during the last 10-15 years. The increasing interest for this subject is associated with its importance in many areas like food industry, pharmaceutical industry, medical science, biochemistry and biochemical engineering.

The adsorption of macromolecules is an extremely complicated phenomenon and as a consequence sophisticated theories are needed to give a full description of it.

The starting point of most theories (8) is that the molecule is adsorbed in trains of segments on the interface and the loops and tails are free in the solution (see figure 2). The first theories developed assumed uncharged polymers (Simha et al 9, Silberberg 10, 11, Hoeve 12, Roe 13). These theories considered the segment-surface interaction and the conformational statistics of the adsorbed molecules while segment-segment and segment-solvent were neglected. In more recently developed theories these interactions are taken into account (Hoeve 14, 15, Silberberg 16, Roe 17, Scheutjens and Fleer 18, 19).

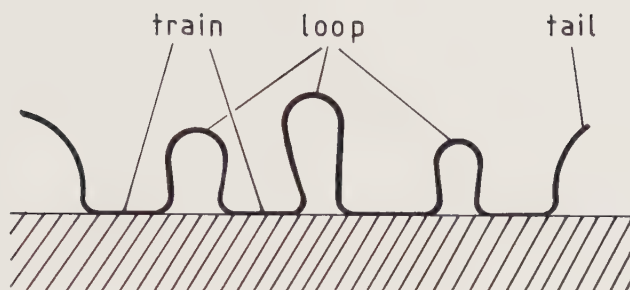


Fig. 2 Conformation of an adsorbed molecule with loops, trains and tails.

In the case of polyelectrolytes the situation becomes more complicated. The most comprehensive theoretical study on this subject was done by Hesselinik (20,21). He extended the treatment done by Hoeve (22) by incorporating electrostatic terms. Adsorption of rigid compact polymeres like proteins makes the situation even more complicated. The statistical calculation used for the description of the segments of flexible polymers can not be applied to the three dimensional structures of the proteins. There is yet no available theory that fully describes protein adsorption and the studies presented give only the general features of the process (Norde and Lyklema 23, MacRitchie 24).

From the literature on protein adsorption some general trends concerning the nature of the adsorption process can be seen but there are also many controversial issues and exceptions which reflect the complexity of this phenomenon.

Due to their amphiphilic nature proteins have high affinity to adsorb on interfaces. When the surface is hydrophobic apolar surface interactions seem to dominate while for

hydrophilic surfaces it is the polar interactions that are of major importance (Norde 25). Usually the proteins have higher affinity for hydrophobic surfaces (Macritchie 26).

The irreversibility of the adsorption process is still not fully understood (Van der Scheer 27). As the proteins are attached to the surface with many segments desorption necessarily requires that all segments leave at the same time which is statistically highly unlikely. Thus, under normal conditions the protein adsorption is irreversible although each segment can adsorb reversibly.

Desorption from hydrophobic surfaces seems to be very difficult to attain. But it is often possible to remove the proteins, to some extent, from hydrophilic surfaces by subjecting them to high pH, high ionic strength, or other extreme conditions. Sometimes the protein can be removed or replaced by a competitive adsorption of another protein having higher affinity for the surface.

The proteins usually retain their compact structure upon adsorption (Lyman et al 28, Morrissay and Stromberg 29, Norde 30). Changes in structure are more probable if the globular structure in the solution is stabilized with hydrophobic bonds (Birdi 31).

Protein adsorption isotherms usually present plateau values at low concentration ($< 0.1\%$). The plateau value is normally within the range of 1 to 5 mg/m² which corresponds to a monomolecular layer of the protein (Norde 32). Sometimes the isotherms present two steps. Such behaviour is usually related to structural changes in the adsorbed layer (Fair and Jamerson 33) or by formation of a second adsorption layer (Mathot and Rothen 34).

Adsorption measurements at concentrations much higher than that corresponding to an established plateau value are usually not performed. Macritchie (26) found that when exposing hydrophobic silica to an 1% BSA solution over 20 mg/m² was adsorbed.

Higher concentrations comparable to those we find at the surface of ultrafiltration membranes are never considered. As will be seen in section 5.3 solute-surface interactions at high concentrations are of great importance and need much more attention.

The influence of the environment can have a strong effect on the adsorption process. The effect of temperature is usually insignificant. The ionic environment can on the other hand have a large influence on the adsorption. When electrostatic factors are the most important for the adsorption, an increased ionic strength decreases the adsorption (Froehling et al 35). In the case where the protein and the surface have the same charge, increasing ionic strength is expected to screen the charge and thus promote adsorption.

The charge density of both the solute and the surface affect the adsorption. Usually an increase in ionization decreases the amount adsorbed (Böhm 36). The influence of the charge density is less pronounced when the non-ionic adsorption is relatively large.

Sorption isotherms of proteins when plotted against the pH of the solution usually show a maximum around the I.E.P. of the protein. The decrease in the adsorption on both sides of the I.E.P. is attributed to deformation of the protein structure (Norde and Lyklema 37, 38).

The studies of the kinetic of the adsorption process are rather limited. The kinetics is found to be dependent on both the surface and the substrate. The adsorption process is usually found to be diffusion-limited and as a consequence an increase in concentration increases the rate of the adsorption (Van der Scheer 27, Gorman et al 39, Bornzin and Miller 40). Kim and Lee (41) observed that the flow rate of the solution had an influence on the adsorption. They found the amount adsorbed to increase with increasing flow velocity for the adsorption of albumin or poly-(dimethyl siloxane) surfaces while the adsorption on copoly-etherurethan-urea showed no dependency on the flow rate of solute.

4. STUDIES OF ADSORPTION FOULING IN UF

Macromolecular fouling of ultrafiltration membranes has been studied quite intensively during the last ten to fifteen years. These studies have resulted in several models used to describe the flux behaviour. According to these models the flux is either said to depend on the hydraulic resistance of a gel layer formed on the membrane when the concentration at the membrane surface exceeds the solubility limit of the macromolecule or depend on the osmotic pressure of the concentrated macrosolute (paper I). None of these theories takes into account interactions between the macrosolute and the surface at concentrations below the gel concentration.

There are numerous observations in the literature reporting that unexpected behaviour in the ultrafiltration process may be caused by macromolecular adsorption on the membrane surface. Lopez (42) observed, when ultrafiltrating dilute solutions of BSA in a rotating membrane module at high rotational velocities in absence of any detectable concentration polarization, that there was some additional resistance besides the resistance of the membrane. This resistance was attributed to the adsorption of the BSA molecules on the membrane surface. Busby and Ingham (43) found that the rejection of polyethylene glycol increased when human serum albumin (HSA) was present in the solution. The HSA was also found to cause irreversible reduction in membrane permeability.

Ingham et al (44) measured the flux as a function of continuously increasing albumin concentration. The sharp decrease in flux between 0.001 and 0.01 mg/ml was attributed to adsorption of protein on the membrane surface. The linear decrease in flux at higher concentrations (> 0.5 mg/ml) was assumed to be caused by concentration polarization or/and by formation of gel on the surface. They also measured the amount accumulated on the membrane surface by measuring changes of concentration in the solution during filtration. They found that the amount increased with increasing applied pressure to give a maximum of approximately $2\ 000\ \text{mg/m}^2$.

(Howell and Velicangil 45) studied the ultrafiltration of papain and BSA. They postulated three major steps in the filtration process. In the first step the concentration profile is built up over the membrane surface. This step takes less than 5 s. The second step accounts for the sharp decrease in flux during the next 10 minutes. The authors states that this flux reduction is caused by the adsorption of the proteins on the membrane surface. The third step is assumed to be dominated by gel formation on the membrane surface. The permeate fluxes from cheese whey filtration by membranes that have been exposed to papain proteins were compared with unexposed membranes and the flux drop due to adsorption was found to be in the range 35-50%.

The same authors (46) measured the amount of papain that adsorbed on the membrane surface by mass balance of the protein solution when exposing it to 1.0 mg/ml concentration without any filtration. At pH 6.2 the amount adsorbed was in the range 680 to 880 mg/m^2 while at pH 4.0 the amount was found to be 48 mg/m^2 .

Fane et al (47) studied the influence of the ionic strength and the pH on the ultrafiltration of BSA protein solution. After ultrafiltration the membranes were rinsed with distilled water and it was assumed that the adsorption layer consisted of the remaining proteins. The permeability after rinsing was measured and the protein left on the membrane was removed with SDS and measured by the Lowry method. Close relationship between the reduction in permeability and the amount adsorbed was obtained. The effect of the pH on the amount adsorbed showed that a maximum was obtained around the I.E.P. The presence of salt was found to increase the adsorption.

For Amicon PM30 membranes the amount adsorbed at pH 5.5 was around 500 mg/m^2 when no salt was present while it was over 1 000 mg/m^2 when the solution was 0.2 M NaCl. When studying (48) membranes that are partially permeable to the solute (BSA) the amount adsorbed was found to be only a little higher. The permeability was on the other hand found to be more affected than for the nonpermeable membranes, probably due to pore plugging. The increase in protein

rejection with time was explained by gradual pore blocking caused by the adsorption of proteins inside the pores of the membrane.

Nichols and Cheryan (49) observed when ultrafiltrating full-fat soybean water extracts and defatted soy flower extracts that the protein content in the final product was less than expected. This was attributed to the adsorption on the membrane. The amount accumulated protein was estimated by mass balance and was found to increase with increasing bulk concentration and to be around $120 - 160 \text{ g/m}^2$ for a bulk concentration of 8-12%.

Le (50) observed that when the membranes were exposed to 0.5% ovalbumin solution for 10 minutes the rejection of PEG increased from 20% to 75% while the reduction in flux was only 7%. After ultrafiltration in 10 min the reduction in flux was 25% but the rejection had increased to 95%. This behaviour was explained by reduction in the effective pore diameter.

Lange (51) measured the reduction in pure buffer permeability of Amicon XM100 membranes when exposed to solutions of varying BSA concentration. At 0.4% concentration a limiting permeability reduction of approximately 50% was obtained. Permeate fluxes from actual ultrafiltration experiments in a stirred batch cell were compared to the fluxes obtained from the adsorption measurements at a concentration corresponding to the wall concentration in the batch cell. These concentrations were calculated using a one-dimensional film model where the thin film mass transfer coefficient was obtained from a stirred-cell mass transfer coefficient. The actual and the predicted adsorption fluxes showed a good agreement. In the prediction the osmotic pressure was taken into account.

Zeman (52) studied the effect of adsorption on the rejection characteristic and the permeability of membranes that partially reject the solute. When exposing Abcor HFM-100 membrane to 500 ppm concentrations of β -lactoglobulin the changes in flux of pure buffer solution were found to depend on the pH of the protein solution. The reduction in flux had a maximum in the region between pH 3 and 5 which is just below the I.E.P. of the protein.

An increase in the ionic strength of the solution at pH 7 by increasing the phosphate buffer concentration was found to increase the thickness of the adsorbed layer.

5. ADSORPTION STUDIES

5.1 Introduction

As mentioned before in section 3 the adsorption of rigid compact polymers like proteins is an extremely complicated phenomenon and there is no comprehensive theory that gives a full description of it. In the literature there are innumerable studies on protein adsorption on all kinds of surfaces including polymers similar to those in membranes. These studies give a general idea about which parameters are of importance in the adsorption of macromolecules on membrane surfaces. Nevertheless real experiments are necessary as these studies give only the main qualitative trend.

In macromolecular ultrafiltration the adsorption of the macrosolute on the membrane surface is the first step in the fouling process. This adsorption is a thermodynamically spontaneous process that takes place as soon as the contact between the membrane and the solute is established. Like all other macromolecular adsorption phenomena it is expected to depend on solute properties like concentration, pH and ionic strength and the surface characteristics.

In section 4 it was mentioned that Lopez (42) did observe a reduction in permeability which he attributed to surface adsorption of the proteins on the membrane surface. His observation initiated the work presented in paper II which was performed in order to verify whether it was reasonable or not to assume that solute adsorption caused the observed reduction in permeability.

The results of these studies indicated clearly that solute adsorption highly affected the hydraulic permeability of the membrane.

The pH of the solution was found to have a strong influence on the adsorption as can be understood from the fact that at 0.1% BSA concentration the reduction in flux was 11% at pH 6.4 to become 62% at pH 4.7 (the isoelectric point of BSA). No changes in permeability were observed when replacing the protein solution by pure buffer solution which indicated that the adsorption layer was irreversibly bound and could not be removed even at the high shear stress used in the experiments.

When studying the role of macromolecular adsorption in fouling of ultrafiltration membranes it is important to perform the experiments under such conditions that all other factors that could have influence on the fouling or flux reduction are eliminated. In the studies presented in the following sections the membranes have been exposed to protein solutions without any filtration. When doing so all influence of concentration polarization or compaction of the proteins are eliminated and all solute-surface interactions that take place are only due to the contact between the solute and the membrane. The effect of these interactions on the membrane permeability has been verified by measuring the permeability of solute-free buffer solution before and after the exposure of the membrane to the protein solution. The amount of protein that adsorbs on solid surfaces is usually in the range of $\mu\text{g}/\text{cm}^2$. As a consequence sensitive methods are needed to measure the amount adsorbed. In this work radiometric measurements have been used to quantify the amount of protein.

The changes in permeability and the amount adsorbed have been put in relation with each other as well as with the properties of the solute and the membrane surface.

5.2 Experimental

5.2.1 Materials

Water pretreatment. All the water used in the experiments was, unless otherwise indicated, prefiltered through a membrane with a cut off of 1 000 daltons after being distilled and deionized

This prefiltration was used since, as it has been shown that distilled and deionized water can still contain impurities such as dust particles and bacteria which can plug the membrane and cause a reduction in flux (51). To prevent bacterial growth 0.02% sodium azide was added to the water before prefiltration.

Bovine serum albumin solutions. The BSA protein used in the experiments was obtained from Sigma Chemical Company product no. A7511. These albumins are prepared from crystallized and lyophilized albumin with 97-99% purity which have been processed to be essentially free of fatty acid (less than 0.005%). The pH of the solutions were adjusted with either 0.01M hydrochloric acid solution or 0.01M sodium hydroxide solution. The solutions were agitated strongly during the pH adjustment to avoid protein denaturation. The salinity of the solutions was made up with analytical grade NaCl. The concentration of the BSA solution was measured in a UV spectrophotometer at 278 nm. All solutions were stored in a refrigerator and used within a week.

Membranes. The membranes used have been listed out in paper III and are here referred to by the same number as they have in that paper. They are all commercially manufactured membranes made out of the polymers most commonly used. The membranes were soaked and flushed with pure buffer solution in order to remove the chemicals used to preserv them. Otherwise no other pretreatment was used.

5.2.2 Hydraulic resistance measurements

The experimental set-up and performance is described in details in each paper. The fluxes in the adsorption measurements are usually presented on a relative basis, i.e.

$$RF = J_A / J_O$$

where RF is the relative permeate flux, J_A = permeate flux after adsorption and J_O = permeate flux of pure buffer solution before

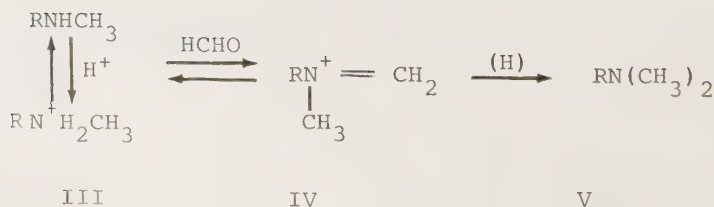
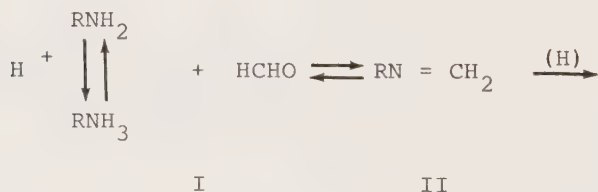
adsorption. J_A and J_O are measured at the same pressure and temperature. The relative resistance of the adsorbed layer R_A/R_M where R_A and R_M are the resistance of the adsorbed layer and the membrane respectively can be given in terms of relative flux by the expression

$$R_A/R_M = 1/RF - 1$$

The main reason for using relative fluxes and relative resistances is that the adsorbed layer can be seen as a resistance in series with the pores of the membrane. As the pores, which cover only a few percentage of the membrane surface, vary in density even between two pieces cut out of the same sheet of membrane the absolute flux is different but the reduction due to adsorption is the same on a relative basis.

5.2.3 Labelling of BSA

In the measurements of the amount adsorbed on the membrane surface ^{14}C labelled BSA proteins were used. The proteins were labelled (53) through reductive alkylation of the protein amino groups with ^{14}C -formaldehyde obtained from New England Nuclear. The reactions that take place are the following (54)



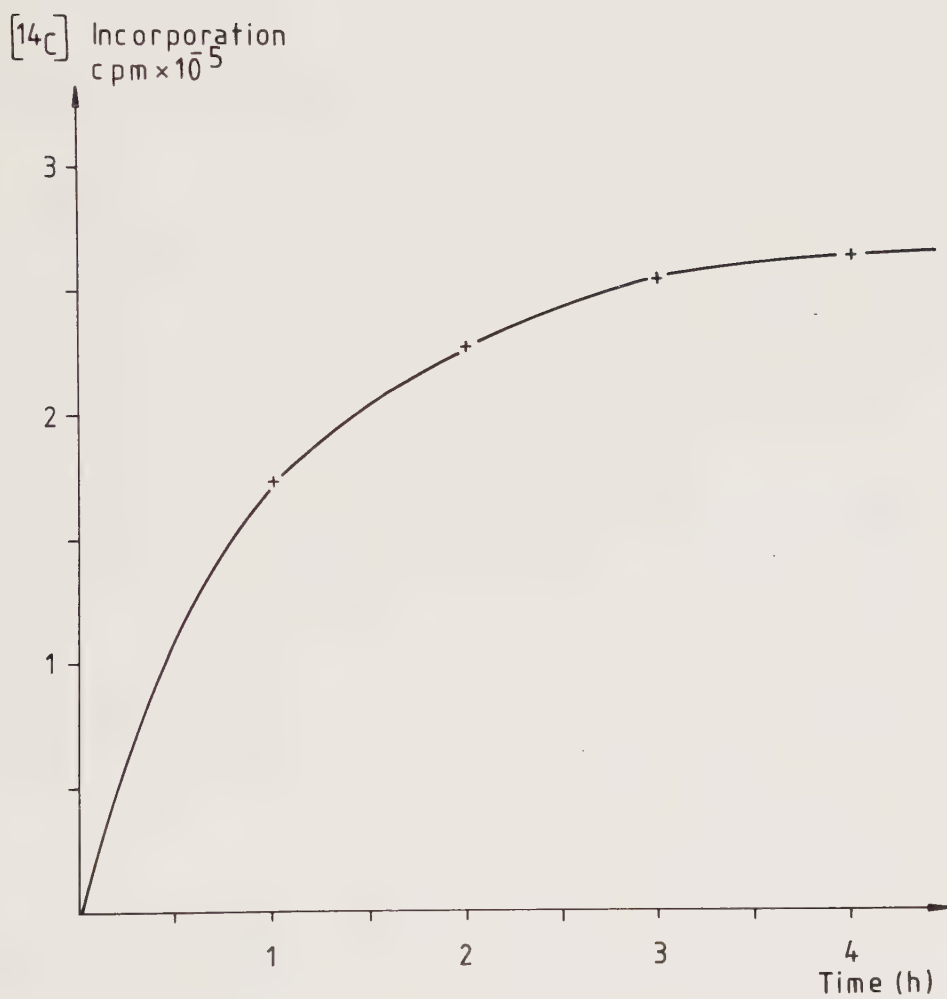


Fig. 3. The effect of time on the amount of (^{14}C) incorporation into BSA. The reaction mixture consisted of 240 μl of 0.625 mg/ml BSA solution containing 30 μCi of (^{14}C) formaldehyde. Aliquots of 5 μm were removed and analyzed at each time.

As can be seen from these reactions the methylated proteins contain both ϵ -N methyl (II) and ϵ -N,N-dimethyl (IV) residues where the latter usually predominates.

This labelling procedure is mild in its effects on proteins and gives minimal changes in gross physical properties. The protein maintains both the total charge and its spacial distribution (55).

The labelling procedure is given in detail in paper III and IV. To find out how much time is needed for incubation in order to get maximum amount of (^{14}C) label incorporated into the protein, the time dependency was studied, figure 3. As can be seen maximum incorporation is obtained after approximately 3-4 hours. As the ^{14}C labelled formaldehyde is expensive it is important to incorporate as high fraction of it as possible. This can be done by increasing the concentration of the protein in the reacting solution. As the specific activity decreases with higher concentration used there is a limit for how high concentration can be used. Figure 4 shows measurements of the specific activity and the yield of formaldehyde obtained as a function of concentration. These results show that the specific activity decreases approximately ten times when going from 0.0625 - 2% while the yield of incorporated HCOH increases four times. The specific activity obtained for 2% BSA in the reacting mixture is about 1×10^7 cpm/mg. This specific activity is high enough for measuring monomolecular layers of BSA on 10 cm^2 membrane area.

5.3 Concentration dependency of the adsorption

It has been mentioned in chapter 3 that proteins adsorb at almost any interface including membranes. This is a thermodynamically spontaneous process that takes place already at low concentrations independent of if there is any transmembrane flux or not. Sorption isotherms usually show plateau values at concentrations less than 0.1 g/100 ml. Adsorption studies at higher concentrations are rare and those concentrations found at the membrane surface in ultrafiltration are never considered in the literature. As the whole concentration range is of interest in the ultrafiltration process sorption isotherms have been studied at both low and high concentrations.

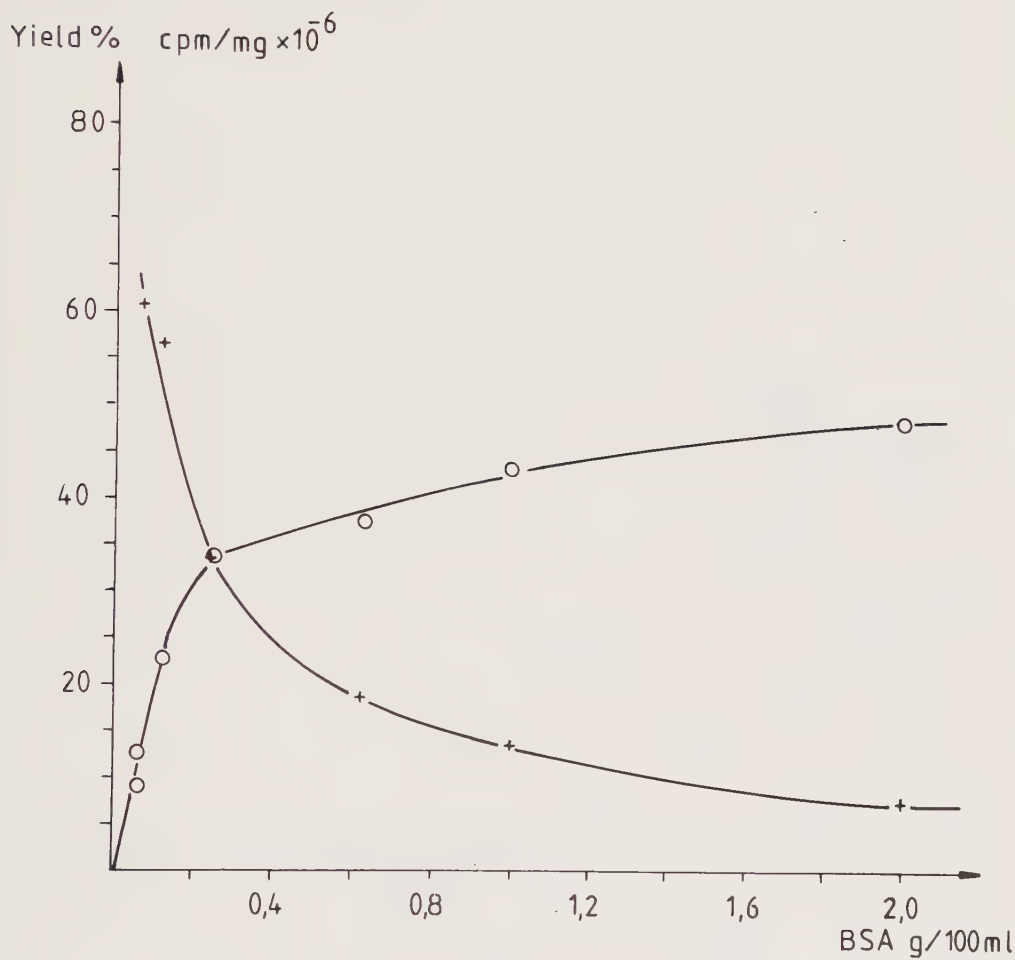


Fig. 4 Specific activity + and the yield o of formaldehyde as a function of BSA concentration in the reaction mixture. Concentration of (^{14}C) label is $0.125 \mu\text{Ci}/\mu\text{l}$.

5.3.1 *Adsorption at low concentration*

In paper III sorption isotherms at low protein concentration (below 1.2 g/100 ml) are presented. In these experiments the membranes have only been exposed to the protein solutions without any filtration. All isotherms have the same characteristic shape observed in other adsorption studies (32) showing increasing adsorption with increasing concentration to form a plateau or a semiplateau at higher concentration.

As discussed in paper III three items are of main interest with regards to these sorption isotherms. First, a semiplateau is formed in the region between 0.05 and 0.2% concentration which indicates two different steps in the adsorption process in the concentration range considered. Secondly and thirdly the amount adsorbed and the difference in adsorption between membranes. The amount adsorbed in the first step is within the range of reported values in the literature (32). Higher up in concentration the amount adsorbed on the polyamide and the two of the polysulfone membranes increases considerably and corresponds to multimolecular layers of BSA. The amount adsorbed on the cellulose acetate membrane and one of the polysulfone membranes is on the other hand close to the surface concentration for close packed monolayers of adsorbed globular molecules of BSA (26). Comparison between the amount adsorbed on the membranes can be seen in figure 5 which reflects the differences between them all.

The roughness of the membrane surface may have an influence on the adsorbed amount as the true surface area differs from the apparent one. This would only cause proportional difference in adsorption between membranes at all the concentration range which is not the case here. It is therefore most likely that the cause of this unequality in adsorption is the surface characteristics of the membranes.

The reduction in permeate flux of pure buffer solution is directly related to the amount adsorbed as can be seen in paper III. The hydraulic resistance of the adsorbed layer causes up to 35% losses in permeability for the membranes that adsorb most protein. The cellulose acetate membranes on the other hand loose only 5% of

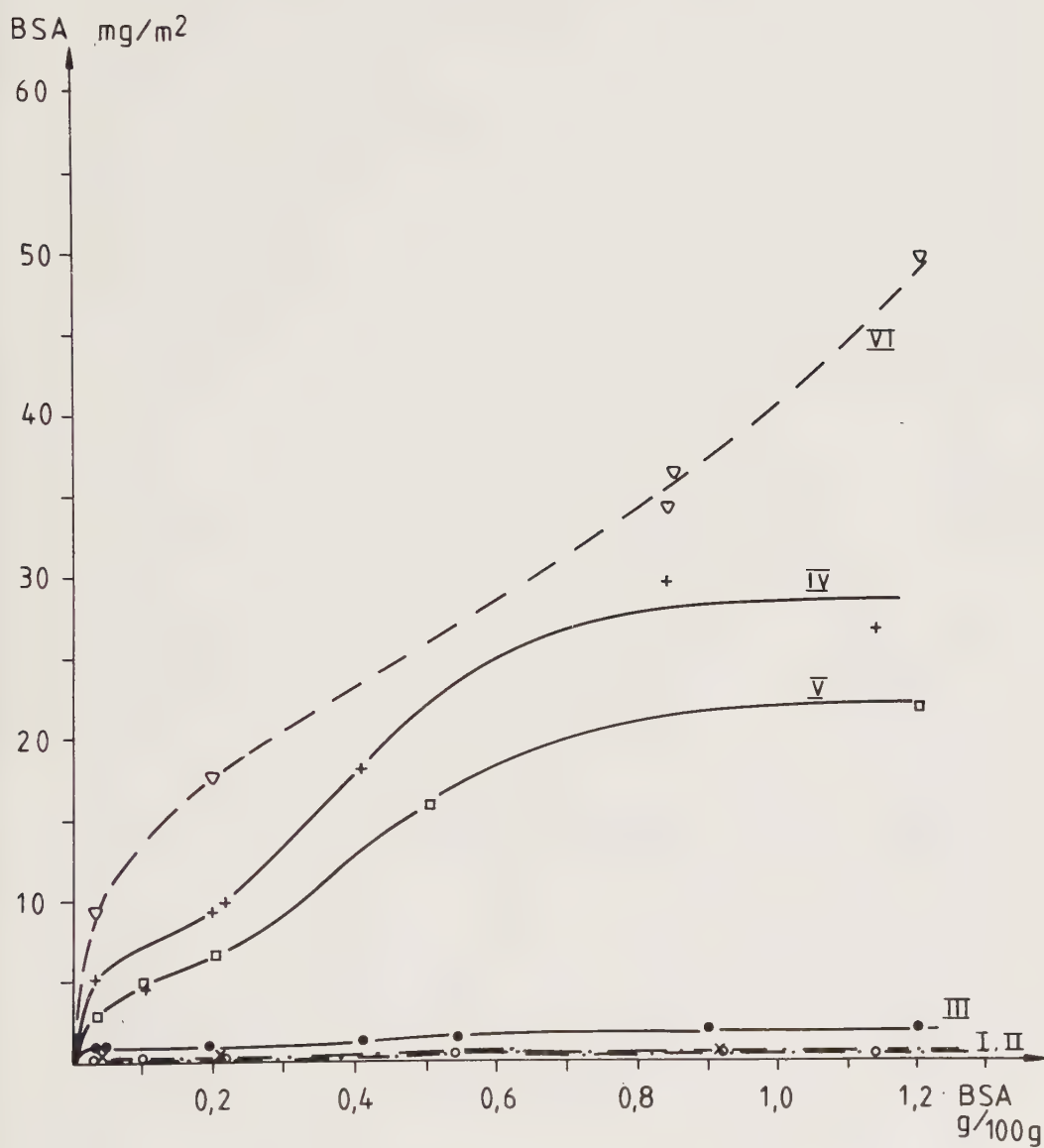


Fig. 5 Adsorption isotherms for BSA on UF-membrane surfaces (pH 7.0, 25°C , 3 hr).

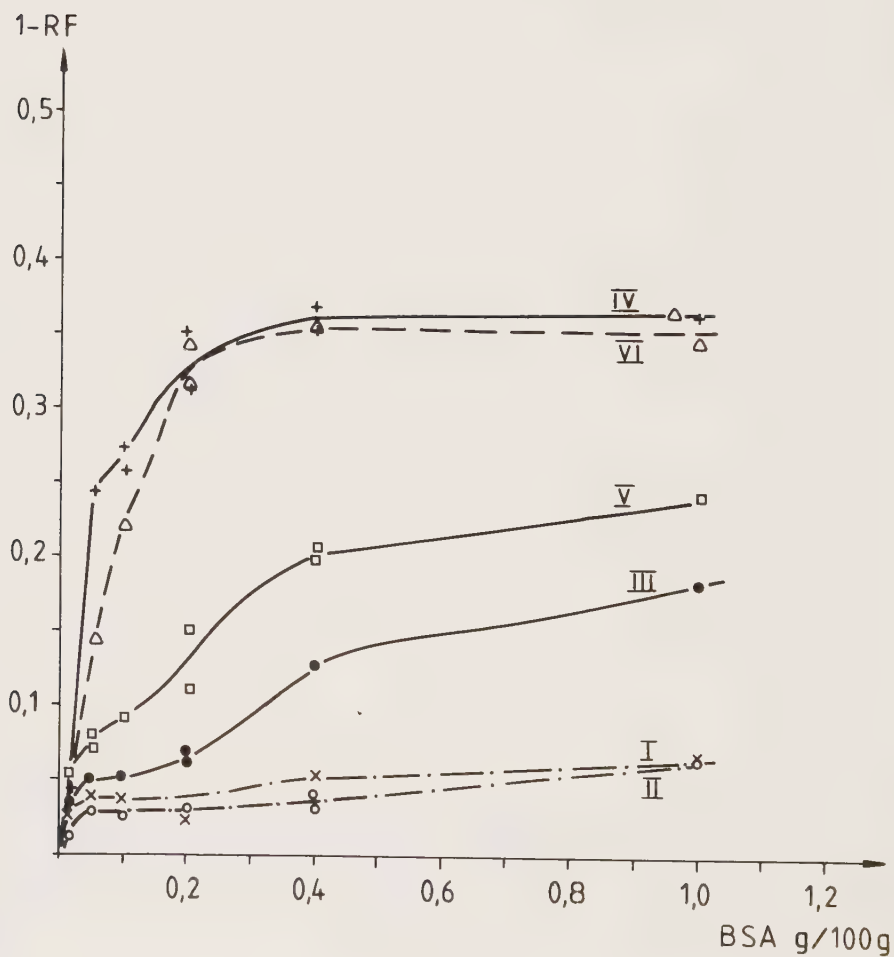


Fig. 6 Influence of the BSA concentration on the relative flux reduction in filtration of a pure saline water solution (0.15 M NaCl, pH 7.0 and 25°C). The BSA solutions have been exposed to the membranes without filtration for 3 hr.

their permeability. In figure 6 the flux reduction of the membrane versus the BSA concentration that has been in contact with the membranes are shown. No direct relationship between the pore size or the molecular cut off and the reduction in flux have been indicated. The two cellulose acetate membranes with molecular cut off of 6 000 and 20 000 show almost exactly the same behaviour. The polysulfone membrane having cut off 6 000 shows less reduction in flux than the two having cut off 20 000. But as the difference in flux reduction between the two more open membranes is greater than between one of them and the one with cut off 6 000 this can not be related to the pore size of the membranes.

5.3.2 *Adsorption at high concentration*

Studies of adsorption isotherms at high concentrations are presented in paper IV. Here as in the measurements at low concentration the membranes have only been exposed to the protein solution and no filtration has been performed. The plateaus or semiplateaus obtained in the adsorption isotherms at low concentration for the hydrophobic polysulfone and polyamide membranes remain up to around 15 to 20 g/100 ml BSA concentrations. In this interval the increase in adsorption is only moderate. Higher up in concentration the amount bound to the membrane increases considerably and this accumulation process of multimolecular layers of proteins looks more like some kind of surface coagulation process than a surface adsorption process. The high amount of protein bound to the membrane between 40 and 50 g/100 ml BSA concentration (800 - 1100 mg/m²) is on the same level as found by Howel and Velicangil (45) and Fane (47). The reasons for this large increase in adsorption at higher concentration can be numerous. As has been mentioned before in chapter 3 the adsorption depends very much on the properties of the protein in the solution. When the concentration in solution is high, molecular interaction increases. This can make it thermodynamically more favorable for the solute to adsorb at the interface. Aggregation of proteins at higher concentration is another factor that could act in favour of increased adsorption.

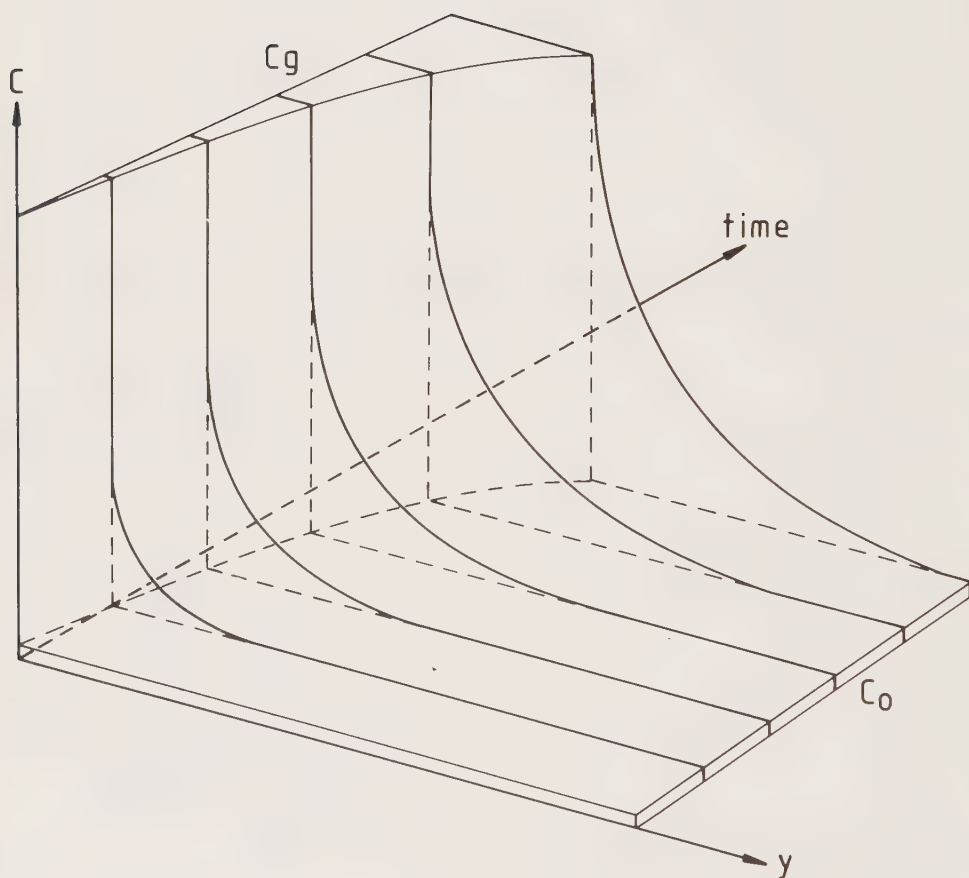


Fig. 7 A schematic illustration of the build-up of the protein layer on the membrane surface.

The increase in adsorption or surface coagulation at higher concentration indicates that the so called "gel layer" is not formed as soon as the concentration at the wall has reached the saturation concentration of the protein (around 58 g/100 ml) but rather gradually over the whole concentration range. This can be described schematically by figure 7.

Opposed to the hydrophobic polysulfone and polyamide membranes the hydrophilic cellulose acetate membranes show no increase in protein adsorption at higher concentrations. This indicates that the surface characteristics is of great importance and the adsorbed layer formed at low concentration is more or less inert to further adsorption. Accordingly the free energy of adsorption is not high enough to exceed the minimum energy needed. This kind of surface characteristic may be of importance when preventing fouling in ultrafiltration.

The reduction in flux due to the surface adsorption or coagulation is related to the amount bound to the membrane in a way similar as in the low concentration measurements. The reduction in permeability obtained below 1 g/100 ml is more or less the same up to about 20 g/100 ml. The large increase in adsorption above this concentration causes exponential decrease in permeability.

5.4 Influence of air on the adsorption

If the membrane surface is not covered with the buffer solution when the protein solution is supplied to the cell a considerable increase in adsorption is observed (paper III). In measurements of protein adsorption at liquid/air interfaces unfolding of the proteins has often been observed (56, 57).

This could partly explain the increase in adsorption mentioned above since when the protein solution is supplied to the cell where the membrane is in direct contact with air a three phase contact of solid/liquid/air is established. The contact between the membrane surface and the partially unfolded proteins is expected to increase the adsorption. The fact that the membrane surface is more hydrophobic when it is in contact with air than when

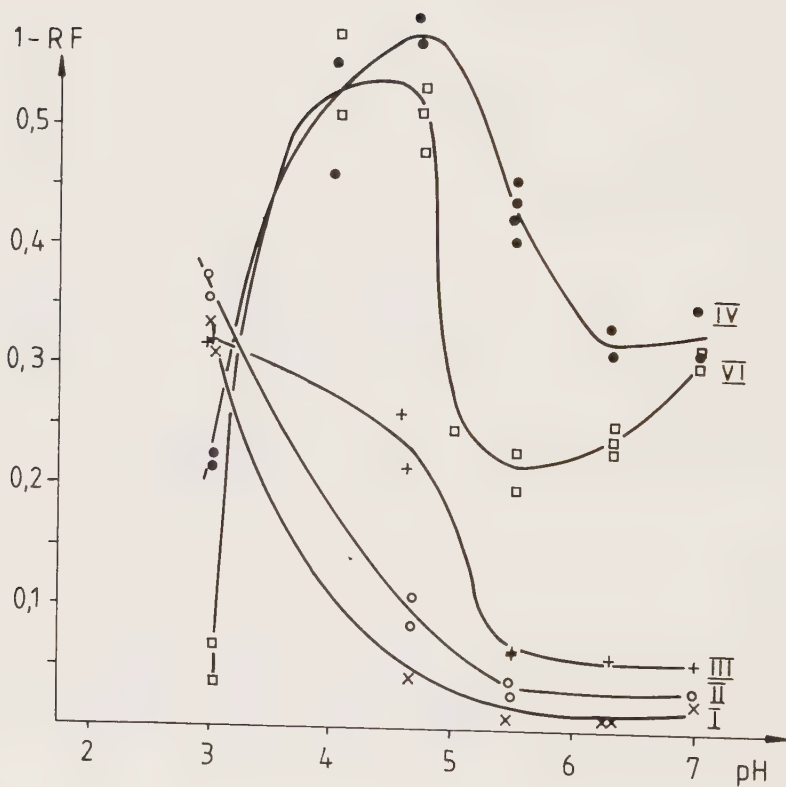


Fig. 8 Influence of pH of the BSA solution exposed to the membrane on the relative flux reduction.

it is covered with buffer solution can also contribute to this increase in adsorption.

This effect could have influence in ultrafiltration if the membrane module is filled with air instead of water when the macromolecular solution is applied. Air bubbles in the feed solution could have similar effects if they penetrate through the boundary layer all the way to the membrane surface.

5.5 pH dependency

In chapter 3 the pH dependency of the adsorption was discussed and it was shown that it highly affects the amount adsorbed. This behaviour is very important in membrane filtration as this variation can have strong influence on the transmembrane flux.

In paper III some results over the pH dependency are presented for membranes I to III. As expected the pH was found to have large effect on both the amount adsorbed and the reduction in permeability. The adsorption increased continuously when going from pH 7 to pH 3.

This behaviour could be explained, as discussed in paper III, by the fact that the BSA protein as well as the membrane are negatively charged above the isoelectric point (pH 4.7). The repulsive forces should therefore decrease when going from pH 7 to pH 4.7. Below pH 4.7 the proteins become positively charged opposite to the membrane so the electric forces become attractive in this interval. This can explain to some extent the higher amount adsorbed at pH 3 than at pH 4.7. Another factor that also can have an influence is the change in the structure of the proteins that take place at pH below 5.

In figure 8 the influence of pH on the adsorption of BSA on the hydrophobic membranes IV and VI is presented together with the results in paper III. The same behaviour is observed for these two membranes when the pH is decreased from pH 7 to pH 4.7.

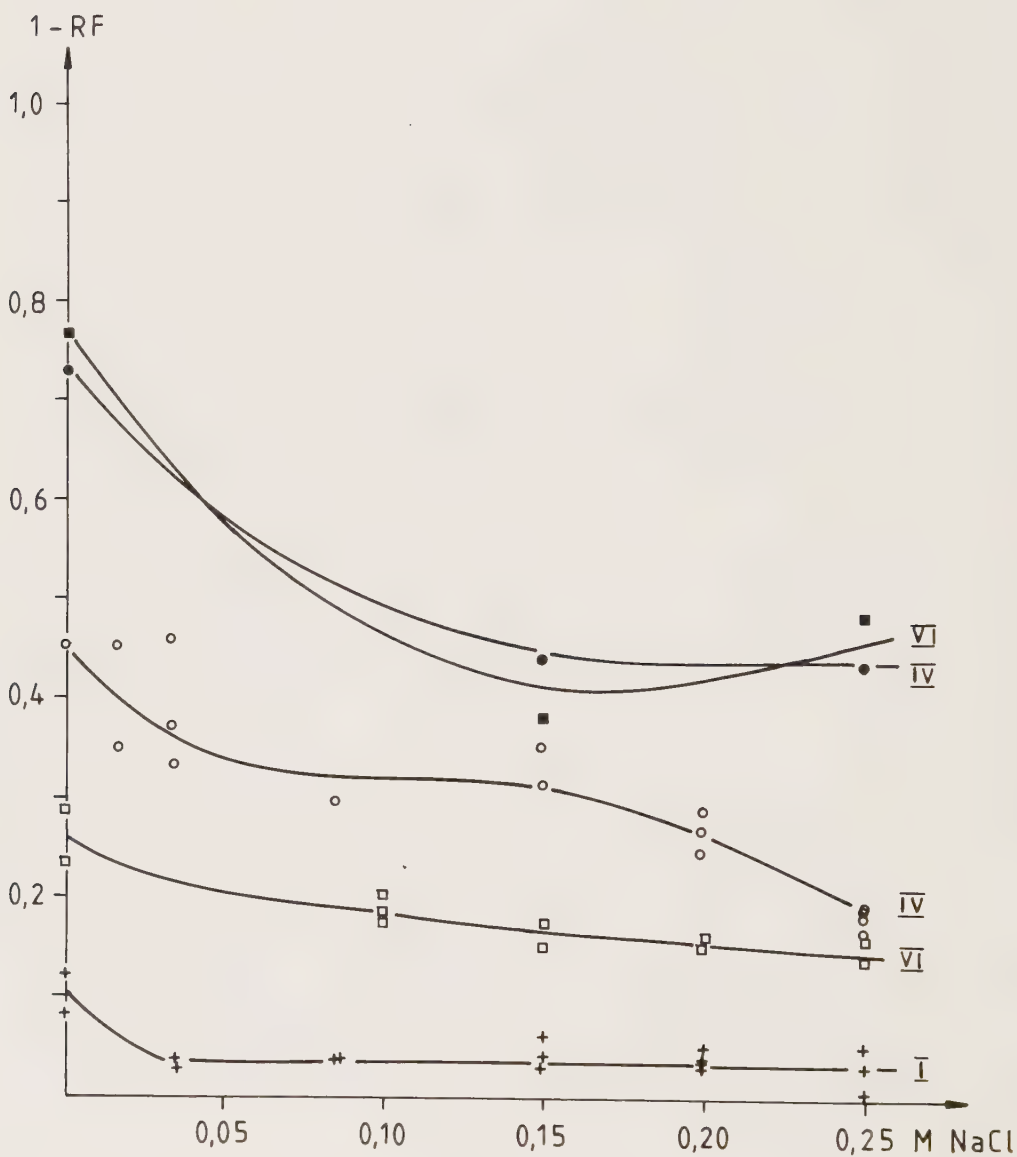


Fig. 9 The effect of the ionic strength of the BSA solution exposed to the membrane on the relative reduction in flux. The concentration of BSA is; 0.2% open symbols, 30% closed symbols.

Below the I.E.P. the hydrophobic membranes act differently and the hydraulic resistance decrease. This indicates that there are some differences between the adsorption mechanisms and that the electric forces are more important for the adsorption on hydrophilic membranes while for the others the hydrophobic interaction between the proteins and the membranes is of greater importance. This behaviour is often observed and one of the explanations used is that even if the proteins are positively charged the negative carboxyl groups in the proteins are oriented towards the surface (32).

5.6 Ionic strength of the solution

In section 3 the influence of the ionic strength on the adsorption was mentioned. From the discussion it appears that the amount adsorbed is sometimes highly affected by the salinity of the solution. This parameter is therefore of importance and could play a main role in the adsorption process.

The reduction in flux due to adsorption of 0.2% and a 30% BSA solution was measured for NaCl concentrations between 0 and 0.25 M. The results are shown in figure 9. As can be seen from these results the effect of the ionic strength on the reduction in flux is rather small at 0.2% BSA concentration. The flux is slightly more affected at 0 M NaCl than at 0.25 M. At 30% BSA concentration, the influence of the ionic strength has the same qualitative trend but it is much more pronounced at 0 M NaCl. This affinity between the BSA molecules and the surface is not in line with the theoretical predictions mentioned in section 3 where it was stated that higher ionic strength should reduce the repulsive electrostatic forces between the negatively charged protein and the negatively charged membrane. This is expected to act in favour of increased adsorption. Similar deviation from the theoretical prediction have been reported by others (25, 27). This indicates that the principal influence of the electrolyte is on the conformational stability of the proteins. The reason for why this effect is much more pronounced at higher concentration could be the fact that the intramolecular electrostatic repulsion, when no salt is in

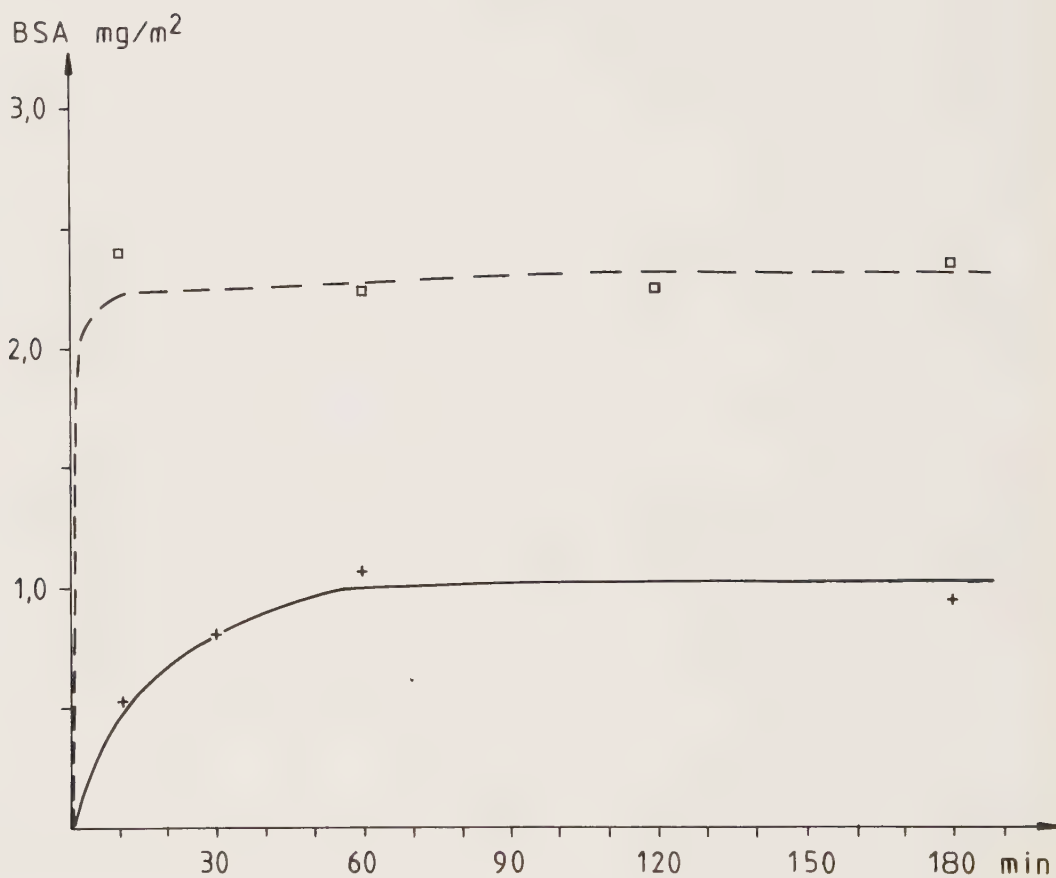


Fig. 10 The time dependency of the amount of BSA adsorbed at the membrane interface (I) from solutions with + 0.027% and □ 0.2% BSA concentration respectively.

the solution, will not be screened as effectively. This effect is expected to contribute to an increase in adsorption specially at high concentration where the distance between the molecules is very short.

5.7 Adsorption kinetics

In paper III some results over the time dependency of the adsorption were presented. In figure 10 and 11 the time dependency is shown for different concentrations. These results show that the adsorption rate increases with increasing concentration. This suggests that the adsorption rate is limited by the movement, in this case diffusion, of solute to the surface and not by some kind of energy barriers. In an ultrafiltration process where there is a convective flow towards the membrane surface, one would therefore expect that the adsorption takes place more or less instantaneously.

5.8 The hydraulic resistance of the adsorbed layer

In chapter 5.3 the amount of BSA adsorbed on the membrane and the decrease in permeability were discussed. The results presented in paper III show that in the region between 0-1 g/100 ml BSA concentration the hydraulic resistance increases most up to about 0.4 g/100 ml whereon the hydraulic resistance is more or less constant up to 1.2 g/100 ml concentration. The resistance of the adsorbed layer formed is found to increase linearly with the amount adsorbed up to a transition stage between the first and the second step in the adsorption where there is a sharp breakpoint. The resistance of the layer formed after this breakpoint, in the second step of the adsorption process, shows also an almost linear relationship but the slope is much lower. From this it can be seen that there is a clear difference between the nature of these two layers. In both cases the specific resistance is constant but it is much higher for the first layer formed than for the second. The reason for this can be either that this first layer blocks the pores of the membrane or, since it is in close contact with the membrane it is more dense than the second one.

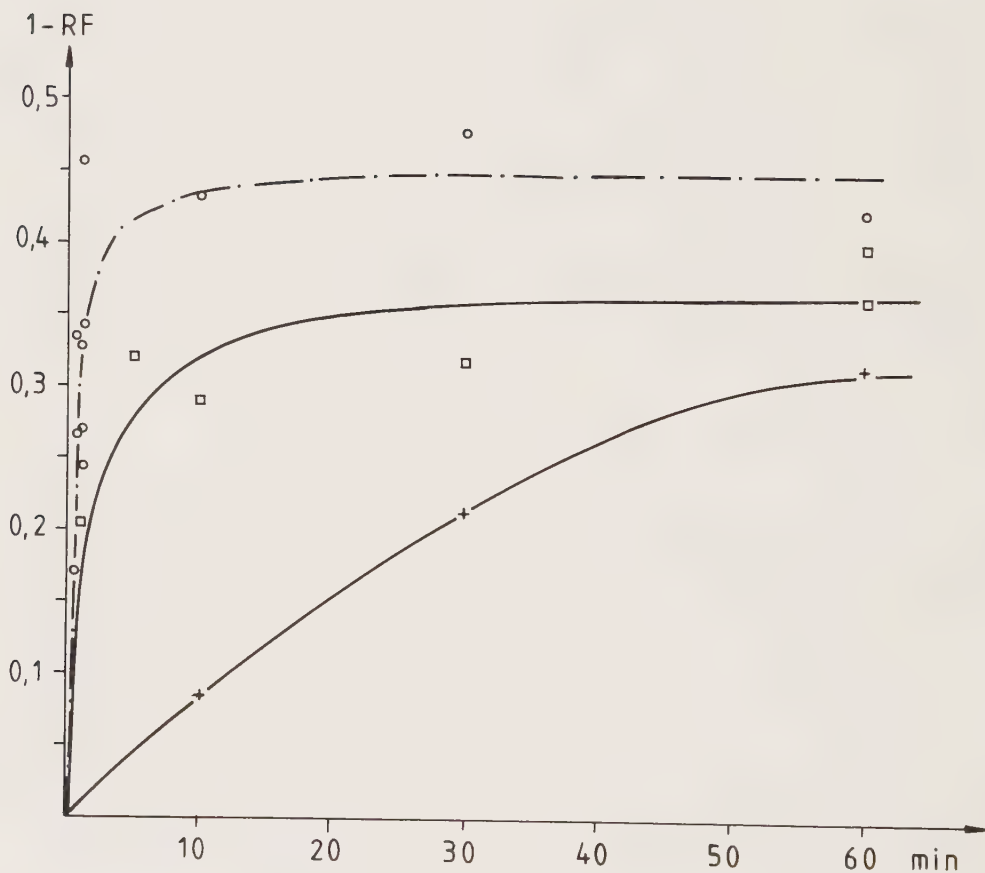


Fig. 11 The time dependency for the reduction in flux due to adsorption of BSA on the membrane surface (IV) from solution with different BSA concentrations; + 0.2%, □ 5%, ○ 25%.

The adsorption measurements at high BSA concentration show that the (pseudo)plateau formed above 0.4 g/100 ml concentration remains up to approximately 20 g/100 ml for the polyamid and polysulfone membranes. At higher concentration the total hydraulic resistance increases markedly due to the large increase in the amount adsorbed in this concentration range as mentioned in section 5.3. The total hydraulic resistance is almost constant for the cellulose acetate membrane as a consequence of that no further adsorption takes place at higher concentration.

The diagram in paper IV (fig. 4) where the relative resistance is plotted versus the amount adsorbed on the polyamide and polysulfone membranes shows that the resistance of the adsorbed layer increases exponentially with increasing adsorption. From the slope of the curve it can be seen that the specific resistance of the adsorbed layer changes continuously. Between 10 and 300 mg/m² the adsorbed layer has a very low specific resistance. Compared to the resistance of the membrane and the first adsorption layer it is almost negligible. Above 300 mg/m² the specific resistance of the adsorbed layer increases successively. This adsorption layer is formed when the wall concentration exceeds 20-30%. The increasing specific resistance indicates that the layer becomes gradually more and more dense as the concentration gets close to the solubility limit of the protein.

In paper IV the relative flux reduction as a function of concentration is experimentally fitted by an exponential equation

$$1 - RF = A + B_1 e^{r_1 C} + B_2 e^{r_2 C} \quad 5.8.1$$

where A corresponds to the (pseudo)plateau obtained below 1 g/100 ml concentration. The first and the second exponential terms account for the decrease in flux at low and high concentration respectively.

The permeate flux in ultrafiltration processes when the reduction in permeability due to adsorption was taken into account is given by the equation

$$J_v = J_o \cdot RF \left(1 - \frac{\sigma \Delta \Pi}{\Delta P}\right) = J_A \left(1 - \frac{\sigma \Delta \Pi}{\Delta P}\right) \quad 5.8.2$$

RF can be obtained from the expression above and Π from osmotic pressure measurements. The validity of this equation will be discussed in chapter 6.

6. ULTRAFILTRATION IN AN UNSTIRRED BATCH CELL

6.1 Prediction of concentration profiles

The results from the prediction of concentration profiles of bovine serum albumin (BSA) in an unstirred batch cell by solving numerically the one dimensional unsteady state convection equation

$$\frac{\partial c}{\partial t} + \frac{\partial (cu)}{\partial y} = \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right)$$

are given in paper V. In these calculations the velocity u was obtained from ultrafiltration experiments while the diffusion coefficient D was taken from the literature.

The numerical solutions show that the concentration profiles and the wall concentration are highly dependent on the diffusion coefficient. This indicates the necessity of reliable values of the diffusivity when solving the equation above. Unfortunately the diffusivity data for protein solutions at high concentration are quite limited and there is an urgent need for more reliable data on the concentration dependency of the diffusion coefficient in the whole concentration interval.

The osmotic pressure is another physical property of concentrated protein solutions that is of interest in ultrafiltration. As mentioned in section 2 the measurements of Scatchard et al (6) and Vilker et al (7) differ quite markedly for concentration above 12 g/100 ml at pH close to 7.

From the experimental flux data and the calculated wall concentration the osmotic pressure can be calculated by using equation 5.8.2 shown in paper V. The comparisons made show that the calculated wall concentrations obtained when using a constant diffusion coefficient of $6.2 \times 10^{-11} \text{ m}^2/\text{s}$ fits best, according to equation 5.8.2, with the osmotic pressure predicted by Scatchard et al (6).

The prediction of the concentration profile using variable diffusion coefficient that fits experimental diffusivity data give calculated osmotic pressure that is somewhat more in agreement with the results of Vilker et al. On the other hand the use of this variable diffusion coefficient in the prediction of the concentration profiles results in wall concentrations that give osmotic pressures according to Vilker et al, that exceeds the applied pressure used in the experiments which is unrealistic.

If reliable osmotic pressure data are available it is possible by comparing the calculated osmotic pressure from equation 5.8.2 with the true experimental one and examine the validity of the diffusion coefficient used in the numerical calculations.

6.2 Secondary hydraulic resistance layer

The measurements of the reduction in flux presented in paper V showed that some secondary hydraulic resistance in series with the resistance of the membrane and the adsorbed layer existed during the unstirred batch cell ultrafiltration. This hydraulic resistance layer has not the same permanent irreversible character like the adsorption layer presented in paper III and IV since it disappears when the protein solution is replaced with pure buffer solution.

This indicates that the secondary hydraulic resistance consists of loosely bound or packed proteins that are easily removed. It is therefore probable that the mechanical stability of this layer is low and under flow condition it is likely removed to large extent by the shear stress at the membrane surface.

6.3 Prediction of permeate fluxes

As pointed out in paper V the equation 5.8.2 can be used to express the permeate flux in ultrafiltration of macromolecules provided that the influence of the adsorption on the permeability and the osmotic pressure as a function of concentration are known. By putting this expression in the one dimensional unsteady state convection equation the flux versus time can be predicted by solving the equation numerically as in the calculation of the concentration profiles.

This kind of calculations are presented in paper V where the concentration dependency term of the osmotic pressure is taken from the results of Scatchard et al. The expression previously obtained in paper IV were used to account for the influence of the adsorption on the hydraulic permeability.

The results show that the numerical calculations with constant diffusion coefficient of $6.2 \times 10^{-11} \text{ m}^2/\text{s}$ fits best with the flux data obtained from unstirred batch cell ultrafiltration experiments. The deviations from the experimental flux data are at the beginning caused by underestimated osmotic pressure values while at longer times where the wall concentration is higher the use of constant diffusivity gives underpredicted values of the diffusion coefficient and thus too high wall concentrations.

Provided that reliable data on the concentration dependency of the adsorption and the osmotic pressure are available the wall concentration can be predicted at any time during an ultrafiltration experiment from equation 5.8.2 with simple iteration calculations. As the flux is depending on the chemical potential at the membrane surface these predictions are valid for both unstirred batch cell systems as well as for flow systems.

7. CONCLUSIONS AND FUTURE ASPECTS

This study indicates clearly that adsorption of macromolecules on the membrane surface plays an important role in the fouling process in ultrafiltration. Already at a concentration below 1 g/100 ml the reduction in flux due to the interaction between the proteins and the membrane surface is in some cases as high as 35%. At higher concentration, close to the solubility limit, 75-80% losses in permeability are observed for the hydrophobic polysulfone and polyamide membranes.

Measurements with ^{14}C -labelled BSA show that the amount adsorbed on these membranes is in the range of few mg/m^2 when the concentration of the BSA solution exposed to them is below 0.4 g/100 ml. The amount adsorbed continuously increases up to values in the range of 1 000 mg/m^2 , when the solute concentration is close to the solubility limit of the protein. This shows that the so-called gel layer is not formed once the wall concentration reaches the solubility limit but rather gradually over the whole solubility range of the protein.

A clear difference in adsorption behaviour is observed between hydrophobic polysulfone and polyamide membranes and the hydrophilic cellulose acetate membranes. The latter do not have an exponential increase in adsorption at high concentration. The amount adsorbed on these membranes reach already at low concentrations of solute protein a maximum value which corresponds approximately to a monomolecular layer of the BSA protein. This indicates clearly that the membrane surface characteristics are of major importance for the adsorption process.

The solution properties have a large influence on the adsorption. When decreasing pH from 7 to the isoelectric point at pH 4.7 both the hydrophobic and the hydrophilic membranes show an increase in adsorption. Below the isoelectric point a different adsorption behaviour is observed as the hydrophilic membranes show an increase in adsorption opposite to the hydrophobic ones. Increasing ionic strength decreases the adsorption. This is more pronounced at high concentration where the protein interaction is stronger.

The adsorption process is found to be primarily diffusion dependent which means that during ultrafiltration, having a convective flow towards the surface due to transmembrane flux, the adsorption takes place almost immediately.

Numerical calculations of the concentration profiles in the unstirred batch cell shows that such profiles are highly dependent on which values are used for the diffusion coefficient. The validity of equation 5.8.2 is found to be reasonable good at predicting the permeate flux time variations for the unstirred batch cell ultrafiltration.

A hydraulic resistance in addition to the resistance of the membrane and the adsorbed layer seems to exist in the unstirred batch cell ultrafiltration. This hydraulic resistance layer is not as firmly bound to the surface as the adsorption layer and therefore disappears when the protein solution is replaced by pure buffer solution.

The work presented in this thesis has given answers to some of the fundamental principles of adsorption in the ultrafiltration of macromolecules. From this some major conclusions can be drawn regarding in which areas the research work has to be concentrated in the future and how the results can be utilized in the best possible way.

The transmembrane flux and the adsorption on the membrane surface are primarily dependent on the chemical potential at the membrane surface. It is therefore important to know how the fluid hydrodynamics influence the conditions in the boundary layer. Studies in this field are necessary both for the optimization of the flow conditions over the membrane and the prediction of the permeate flux.

To this purpose information is needed concerning the build-up of the fouling layer and the concentration polarization layer over the whole entrance region where both the velocity and the concentration profiles are developing as well as in the region where the velocity boundary layer is fully developed. Studies of the

shear stress influence on the fouling layer is also of importance. In section 3 it was mentioned that in some cases higher amounts of protein adsorb when the liquid is flowing over the surface compared to when it is stationary. This indicates that the shear stress can have influence on the adsorption process probably by changing the conformation structure of the protein. This kind of phenomenon could have a large influence on the membrane permeability and must therefore be taken into account. The dependency of the second hydraulic resistance layer, observed in the unstirred batch cell ultrafiltration, on both the concentration and the fluid hydrodynamics also needs further investigation.

Besides what is mentioned above reliable information of physical properties of the macrosolute like diffusion coefficient and osmotic pressure, are necessary for developing and testing the validity of a mathematical model describing the fouling and the flux behaviour in the ultrafiltration process.

Another field of interest is the surface characteristics of the membrane. In this thesis the nature of the surface was found to be of large importance for the adsorption process. Studies of the membrane properties influencing the adsorption process, as well as how the surface can be modified, are therefore of importance. Precoating of the membrane surface with macromolecules which have little influence on the membrane permeability but prevent it from further adsorption is an example of a simple but promising pretreatment.

Another factor associated with the adsorption process is the change in the separation ability of the membrane. This resulting effect of the adsorption is of high importance and needs to be studied in details.

In the work presented in this thesis only well defined solutions of BSA have been used. A next step would therefore be to test other types of proteins as well as other macromolecules. Usually in ultrafiltration the process fluid is a multicomponent mixture of different macromolecules, low molecular weight organic

material and salts. Examples of this type of solutions are milk and milkproducts, and downstream liquids from biotechnical processes. In this case there is also an interaction among molecules in the solution that can influence the adsorption process. Studies with real process liquids are therefore necessary for a complete understanding of the whole fouling phenomenon.

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REFERENCES

1. P.G. Squire, P. Moser and C.T. O'Konski. The Hydrodynamic Properties of Bovine Serum Albumin Monomer and Dimer. *Biochemistry* 7 (1968) 4261-4272.
2. J.R. Brown. *Fed. Proc.* 34 (1975) 591.
3. J.J.S. Shen and R.F. Probstein. On the Prediction of Limiting Flux in Laminar Ultrafiltration of Macromolecular Solutions. *Ind. Eng. Chem. Fundam.* 16 (1977) 459-465.
4. R.F. Probstein, W.F. Leung and Y. Alliance. Determination of Diffusivity and Gel Concentration in Macromolecular Solutions by Ultrafiltration. *J. Phys. Chem.* 83 (1979), 1228-1232.
5. A.A. Kozinski and E.N. Lightfoot. Protein Ultrafiltration. A General Example of Boundary Layer Filtration. *AIChE. J.* 18 (1972) 1030-1040.
6. G. Scatchard, A.C. Batchelder, A. Brown and M. Zosa. Preparation and Properties of Serum and Plasma Proteins. VII. Osmotic Equilibria in Concentrated Solutions of Serum Albumin. *J. Amer. Chem. Soc.* 68 (1946) 2610-2612.
7. V.L. Vilker, C.K. Colton and K.A. Smith. The Osmotic Pressure of Concentrated Protein: Effect of Concentration and pH in Saline Solutions of Bovine Serum Albumin. *J. Colloid Interface Sci.* 79 (1981) 548-566.
8. G.J. Fleer and J. Lyklema. Adsorption of Polymers, in G.D. Parfitt and C.H. Rochester (Eds). *Adsorption from Solution at the Solid/Liquid Interface* (1983) 153-220.
9. R. Simha, H.L. Frish and F.R. Eirich. The Adsorption of Flexible Macromolecules. *J. Phys. Chem.* 57 (1953) 584-589.

10. A. Silberberg. The Adsorption of Flexible Macro-Molecules.
Part I and Part II.
J. Phys. Chem. 66 (1962) 1872-1883, 1884-1907.
11. A. Silberberg. Adsorption of Flexible Macromolecules.
III. Generalized Treatment of the Isolated Macromolecules;
The Effect of Self-Exclusion.
J.Chem. Phys. 46 (1967) 1105.
12. C.A.J. Hoeve. Density Distribution of Polymer Segments
in the Vicinity of an Adsorbing Interface.
J. Chem. Phys. 43 (1965) 3007-3008.
13. R.J. Roe. Conformation of an Isolated Polymer Molecule
at an Interface. II. Dependence on Molecular Weight.
J.Chem. Phys. 43 (1965) 1591-1598.
14. C.A.J. Hoeve. Adsorption Isotherms for Polymer Chains Adsorbed
from Solvents.
J. Chem. Phys. 44 (1966) 1505-1509.
15. C.A.J. Hoeve. On the General Theory of Polymer Adsorption
at a Interface.
J. Polym. Sci. 30 (1970) 361-367.
16. A. Silberberg. Adsorption of Flexible Macromolecules.
IV. Effect of Solvent-Solute Interaction, Solute Concentration,
and Molecular Weight.
J. Chem. Phys. 48 (1968) 2835-2851.
17. R.J. Roe. Multilayer Theory of Adsorption from a Polymer
Solution.
J. Chem. Phys. 60 (1974) 4192-4207.

18. J.M.H.M. Scheutjens and G.J. Fleer. Statistical Theory of the Adsorption of Interacting Chain Molecules. 1. Partition Function, Segment Density Distribution, and Adsorption Isotherms.
J. Phys. Chem. 83 (1979) 1619-1635.
19. J.M.H.M. Scheutjens and G.J. Fleer. Statistical Theory on the Adsorption of Interacting Chain Molecules. 2. Train, Loop, and Tail Size Distribution.
J. Phys. Chem. 84 (1980) 178-190.
20. F.T. Hesselink. On the Theory of Polyelectrolyte Adsorption.
J. Colloid Interface Sci. 60 (1977) 448-466.
21. F.T. Hesselink. Adsorption of Polyelectrolytes from Dilute Solution, in G.D. Parfitt and C.H. Rochester (Eds), Adsorption from Solution at the Solid/Liquid Interface (1983) 377-412.
22. C.A.J. Hoeve. The Theory of Polymer Adsorption at Interfaces.
J. Polym. Sci. 34 (1971) 1-10.
23. W. Norde and J. Lyklema. Thermodynamics of Protein Adsorption.
J. Colloid Interface Sci. 71 (1979) 350-366.
24. F. MacRitchie. Proteins at Interfaces.
Advan. Protein. Chem. 32 (1978) 283-326.
25. W. Norde. Proteins at Interfaces, Ph.D. Thesis, Wageningen University, The Netherlands, 1976.
26. F. MacRitchie. The Adsorption of Proteins at the Solid/Liquid Interface.
J. Colloid Interface Sci. 38 (1972) 484-488.

27. A. Van der Scheer. Adsorption of Plasma Proteins, Ph.D. Thesis, Technische Hogeschool, Twente, The Netherlands 1978.
28. D.J. Lyman, J.L. Brash, S.W. Chaikin, K.G. Klein and M. Carini. The Effect of Chemical Structure and Surface Properties of Synthetic Polymers on the Coagulation of Blood. II. Protein and Platelet Interaction with Polymer Surface.
Trans. Amer. Soc. Artif. Internal. Organs 14 (1968) 250-255.
29. B.W. Morrissey and R.R. Stromberg. The Conformation of Adsorbed Blood Proteins by Infrared Bound Fraction Measurements.
J. Colloid Interface Sci, 46 (1974) 152-164.
30. W. Norde, in L.H. Lee (Ed), Adhesion and Adsorption of Polymers, Part B, Plenum Publ. Co, New York, (1980) 801.
31. K.S. Birdi. Spread Monolayer Films of Proteins at the Air-Water Interface.
J. Colloid Interface Sci. 43 (1973) 545-547.
32. W. Norde. The Behaviour of Biological Materials at Solid/Liquid Surfaces, Physicochemical Aspects in: B. Hallström, D.B. Lund and Ch. Trägårdh (Eds), Proc. from the International Workshop on the Fundamentals and Application of Surface Phenomena Associated with Fouling and Cleaning in Food Processing, Tylösand, Sweden 1981, Lund University Press, 299-308.
33. B.D. Fair and A.M. Jamieson. Studies of Protein Adsorption on Polystyrene Latex Surfaces.
J. Colloid Interface Sci, 77 (1980) 525-534.

34. C. Mathot and A. Rothen. Adsorption of Purified Serum Proteins on Metalized Glass Slides and Their Significance for the Immunoelectroadsorption Method.
J. Colloid Interface Sci. 31 (1969) 51-60.
35. P.E. Froehling, A. Bantjes and Z. Kolar. Adsorption of a Synthetic Heparinoid Polyelectrolyte on an Ion-Exchange Surface.
J. Colloid Interface Sci. 62 (1977) 35-39.
36. J.T.C. Böhm, Thesis, Agricultural University Wageningen, The Netherlands 1974.
37. W. Norde and J. Lyklema. The Adsorption of Human Plasma Albumin and Bovine Pancreas Ribonuclease at Negatively Charged Polystyrene Surfaces. I. Adsorption Isotherms. Effect of Charge, Ionic Strength, and Temperature.
J. Colloid Interface Sci. 66 (1978 a) 257-265.
38. W. Norde and J. Lyklema. The Adsorption of Human Plasma Albumin and Bovine Pancreas Ribonuclease at Negatively Charged Polystyrene Surfaces. II. Hydrogen Ion Titrations.
J. Colloid Interface Sci. 66 (1978 b) 266-276.
39. R.R. Gorman, G.E. Stoner and A. Catlin. The Adsorption of Fibrinogen. An Electron Microscope Study.
J. Phys. Chem. 75 (1971) 2103-2107.
40. G.A. Bornin and I.F. Miller. the Kinetics of Protein Adsorption on Synthetics and Modified Natural Surfaces.
J. Colloid Interface Sci. 86 (1982) 539-558.
41. S.W. Kim and R.G. Lee. Adsorption of Blood Proteins onto Polymer Surfaces in R.E. Bair (Ed).
Applied Chemistry at Protein Interface (Advances in Chemistry Series 145), Washington D.C. 1975.

42. M. López-Leiva, Ultrafiltration in Rotary Annular Flow, Ph.D. Thesis, Lund University, Sweden (1979).
43. T.F. Busby and K.C. Ingham. Separation of Macromolecules by Ultrafiltration: Removal of Poly(ethylene glycol) from Human Albumin. J. Biochem. Biophys. Methods. 2 (1980) 191-206.
44. C.I. Ingham, T.F. Busby, Y. Sahlestrom and F. Castino. Separation of Macromolecules by Ultrafiltration: Influence of Protein Adsorption, Protein-Protein Interactions, and Concentration Polarization, in A.R. Cooper (Ed), Ultrafiltration Membranes and Applications, Polymer Science and Technology, vol 13 Plenum Press, New York 1980, 141-158.
45. J.A. Howell and O. Velicangil. Theoretical Considerations of Membrane Fouling and its Treatment with Immobilized Enzymes for Protein Ultrafiltration. J. Applied Polym. Sci. 27, (1982) 21-32.
46. O. Velicangil and J.A. Howell. Protease-Coupled Membranes for Ultrafiltration. Biotechnol. Bioengr, 19 (1971) 1891-1894.
47. A.G. Fane, C.J.D. Fell and A. Suki. The Effect of pH and Ionic Environment on the Ultrafiltration of Protein Solutions with Retentive Membranes. J. Membr. Sci, 16 (1983) 195-210.
48. A.G. Fane, C.J.D. Fell and A.G. Waters. Ultrafiltration of Protein Solutions Through Partially Permeable Membranes-The Effect of Adsorption and Solution Environment. J. Membr. Sci, 16 (1983) 211-224.
49. D.J. Nichols and M. Cheryan. Production of Soy Isolate by Ultrafiltration: Factor Affecting Yield and Composition. J. Food Sci. 46 (1981) 367-372.

50. M.S. Le. Membrane Ultrafiltration Fouling and Treatment.
Ph.D. Thesis, University College of Swansea, England,
1982.
51. K.E. Lange, Ph.D. Thesis in Chemical Engineering, Stanford
University, California, unpublished results 1983.
52. L.J. Zeman. Adsorption Effects in Rejection of Macromole-
cules by Ultrafiltration Membranes.
J. Membr. Sci., (1983) 213-230.
53. D. Dottavio-Martin and J.M. Ravel, Radiolabeling of Proteins
by Reductive Alkylation with (^{14}C) Formaldehyde and Sodium
Cyanoborohydride, *Analyt. Biochem.* 87, (1978) 562-565.
54. G.E. Means and R.E. Fenney, Reductive Alkylation of Amino
Groups in Proteins.
Biochemistry 7, No 6 (1968), 2192-2201.
55. R.H. Rice and G.E. Means, Radioactive Labeling of Proteins
in Vitro.
J. Biol. Chem., 3 (1971) 831-832.
56. P.R. Musselwhite, J.A. Kitchener. The Limiting Thickness
of Protein Films.
J. Colloid Interface Sci., 24 (1967) 80-83.
57. M.T.A. Evans, J. Mitchell, P.R. Musselwhite and L.J. Irons
in M. Blank (Ed), *Surface Chemistry of Biological Systems*.
Plenum Press, New York (1970) 1.

I

CONCENTRATION POLARIZATION AND FOULING

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CONCENTRATION POLARIZATION AND FOULING

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ABSTRACT

Concentration polarization is often the reason for the serious limitation of the membrane processes due to its negative influence on the transmembrane flux. Many theoretical studies on this polarization phenomena have resulted in mathematical models for concentration polarization. In most of them, solutions are sought for the coupled nonlinear system of the equations of continuity and motion. Each of these solutions makes use of some assumptions in order to simplify the equations which represent the phenomenon.

Different kinds of flow systems have been constructed in order to reduce the concentration polarization. The aim of these flow systems has mainly been to improve the mass transport from the membrane surface back to the bulk solution.

Fouling often is a result of concentration polarization, but can also have other reasons.

The attention that was drawn to fouling ten to fifteen years ago mostly consisted of recognizing the fact as such and to roughly identify the foulant. Later, efforts to avoid the negative effects have basically followed the paths of altering the composition of the feed solution by a pretreatment to change or get rid of the foulant, to change the hydrodynamics of the membrane module or to alter the membrane itself.

However, unveiling the basic mechanisms of fouling attracted little attention until the late seventies when for example fouling of an RO sea water desalination membrane could be subdivided into four consecutive steps.

Also, studies of the chemistry and physics of fouling have been performed on which lately and revealed in closer detail some of the responsible phenomena.

1. INTRODUCTION

In membrane filtration processes some of the components in the solution are rejected by the membrane. Before steady state the convective flow of these components to the membrane surface is bigger than that due to diffusion backflow to the bulk solution. Because of this an accumulation of the rejected component takes place at the membrane surface. This wellknown phenomena is called concen-

tration polarization (CP). It is often a serious problem in membrane operations due to its negative influence on the transmembrane flux. Negative aspects associated with concentration polarization are:

1. An increase in chemical potential at the surface reduces the driving force for the filtration.
2. If the wall concentration of solute reaches the saturation concentration, precipitation or formation of a gel on the membrane surface increases the hydrostatic resistance.
3. High concentration of solute at the membrane interface increases the risks for changes in composition of the membrane material due to chemical attack.
4. The deposition of solute on the surface can change the separation characteristic of the membrane.

As a consequence of all these negative factors the transmembrane fluxes in commercial plants is only 2-10% of the transmembrane fluxes for pure water. Therefore it is extremely important to make some efforts in order to reduce the concentration polarization. However it is not always possible to explain the flux behaviour as a consequence of CP only. Fouling is then said to occur as well.

Fouling is an accumulation of material on the surface of the membrane that decreases the permeate flux. Epstein (77) classifies this phenomenon as

1. Precipitation fouling
2. Particulate fouling
3. Chemical reaction fouling
4. Corrosion fouling
5. Biological fouling
6. Freezing fouling.

This classification is applied to solid heat transfer surfaces but is partly also applicable to membrane surfaces.

Fouling is in some cases an irreversible adsorption of macromolecules while gel formation caused by CP in its true sense is reversible lacking forces between the macromolecules in the gel. In the fouling gel diffusion is hindered by the development of strong attractions between the macromolecules in the gel.

If the gel is also strongly attached to the membrane surface the system is very hard to alter, even by washing procedures.

Another difference is that while the analysis of CP requires essentially mathematics, fouling requires knowledge about physical chemistry as well.

2 CONCENTRATION POLARIZATION

2.1 MATHEMATICAL DEVELOPMENTS

In order to be able to deal with the problem of concentration polarization one must understand the transport phenomena at the membrane-solute interface.

Steady flow reverse osmosis systems are rather well defined from fluid mechanical viewpoint. This means that mathematical analysis using the basic equations of fluid dynamic and convective transport are expected to be reliable. Lots of efforts have been made to develop analytical models to be able to predict the concentration distribution normal to the membrane surface and its influence on the transmembrane flux. In most of them, solutions are sought for the coupled nonlinear system of the equations of change (1):

$$\text{Equation of continuity} \quad \frac{D\rho}{Dt} = -\rho (\vec{\nabla} \cdot \vec{v}) \quad (1)$$

$$\text{Equation of motion} \quad \rho \frac{D\vec{v}}{Dt} = -\vec{\nabla} p - \vec{\nabla} \cdot \tau + \rho \vec{g} \quad (2)$$

$$\text{Equation of continuity for solute} \quad \frac{DC}{Dt} = D \nabla^2 C \quad (3)$$

Each of these models makes use of some assumptions in order to simplify the equations which represent the phenomena. The wall velocity is usually given by the expression

$$J_v = A (\Delta p - \Delta \pi) \quad (4)$$

and the selectivity of the membrane by the rejection parameter R , where

$$R = 1 - \frac{C_p}{C_w} \quad (5)$$

2.1.1 Reverse osmosis system

(i) Unstirred batch cell systems. The most simple reverse osmosis system is the unstirred batch cell. Analytical studies of this kind of systems are primarily of interest for studies of membrane characteristics and for some industrial applications like ultrafiltration of pharmaceutical and biological solutions where the shear stress in the flow system can damage the product. The main objective is therefore to obtain a model that predicts concentration polarization at the membrane surface and the permeate flux as a function of time and operation conditions for a given membrane characteristic. These analysis can be used together with experimental data to determine the membrane constant A and the rejection characteristics R .

In the analysis of unstirred batch cell systems the general assumptions are

that the length of the cylinder is long enough so that any increase in concentration is unnoticeable far away from the membrane surface (Fig. 1). This means that the system becomes semi-infinite. With these assumptions the problem to be solved is the differential equation for the continuity of the solute in the form

$$\frac{dC}{dt} - |J_v| \frac{dC}{dy} = D \frac{d^2 C}{dy^2} \quad (6)$$

with the boundary condition

$$C(0, y) = C_0 \quad (7)$$

$$C(t, \infty) = C_0 \quad (8)$$

$$|J_v| C(t, 0) + D \frac{dC(t, 0)}{dy} = (1-R) |J_v| C(t, 0) \quad (9)$$

The two first boundary conditions state that the concentration is uniform in the whole system at the beginning ($t=0$) and changes in concentration are not noticed at infinity. The third boundary condition gives the mass balance of solute at the membrane surface.

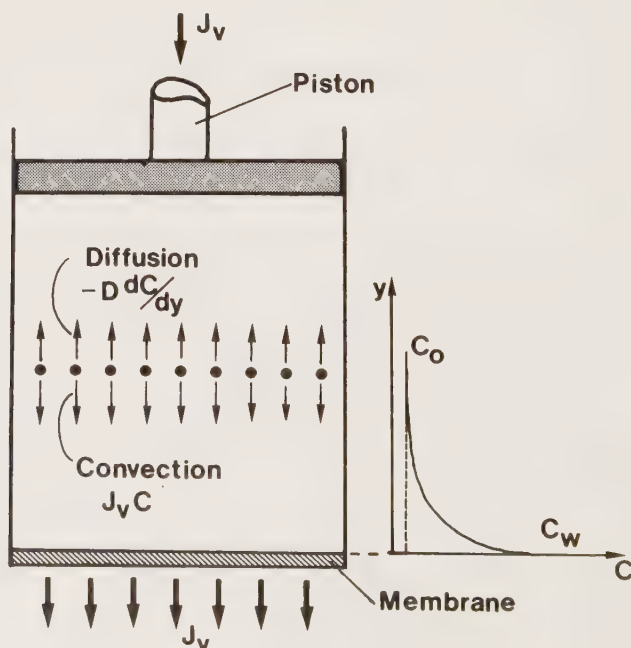


Fig 1. Unstirred batch cell.

Dresner (2) analysed this system mathematically with the assumptions that the osmotic pressure can be neglected ($B = \Pi_0/\Delta p = 0$), which means constant permeat flux, and that the membrane is completely impermeable to solute ($R=1$). In this case the equations above become linear so Laplace transformation can be used to obtain the closed-form solution

$$\frac{C_w}{C_0} - 1 = 1 - \left(1 + \frac{\tau_1}{2}\right) \operatorname{erfc}\left(\sqrt{\tau_1}/2\right) + \sqrt{\tau_1/\pi} e^{-\tau_1/4} + \tau_1 \quad (10)$$

$$\text{where } \tau_1 = \frac{j_{v0}^2 t}{D} \quad (11)$$

This means that the concentration polarization increases linearly with time for large τ_1 .

Raridon et al (3) extended this analysis to be valid for nonideal membrane ($0 < R \leq 1$). By using Laplace transformation they got the solution

$$\begin{aligned} \frac{C_w}{C_0} - 1 = & \frac{1}{1-R} \left[R - \emptyset (2R-1) e^{\tau_1 R(R-1)} \right] + \\ & + \frac{1}{2(1-R)} \left[|2R-1| e^{\tau_1 R(R-1)} \operatorname{erfc}\left(\frac{\sqrt{\tau_1}}{2} |2R-1|\right) - \operatorname{erfc}\left(\frac{\sqrt{\tau_1}}{2}\right) \right] \end{aligned} \quad (12)$$

$$\text{where } \emptyset = 1 \quad R \geq 0.5$$

$$\emptyset = 0 \quad R < 0.5$$

Liu and Williams (4) did also extend this analysis by using Laplace technique to get a solution over the entire concentration field which accounts for all R and B in the following form

$$\begin{aligned} \frac{C}{C_0} = & 1 + \frac{R}{2(1-R)} e^{-\eta} \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\tau'}} - \frac{\sqrt{\tau'}}{2}\right) - \frac{1}{2} \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\tau'}} + \frac{\sqrt{\tau'}}{2}\right) - \\ & - \frac{2R-1}{2(1-R)} \exp\left[-R\eta - R(1-R)\tau'\right] \operatorname{erfc}\left[\frac{\eta}{2\sqrt{\tau'}} - (2R-1)\frac{\sqrt{\tau'}}{2}\right] \end{aligned} \quad (13)$$

$$\text{where } \eta = \frac{A(\Delta p)y_1}{D} (1-RB) \quad (14)$$

$$\tau' = \frac{A^2(\Delta p^2)y_1}{D} (1-RB)^2 \quad (15)$$

The value of τ' at which the equation above breaks down increases as B decreases. This equation is therefore most useful when $B \ll 1$. Mahlab et al (142) have done a similar analysis where they got another set of solutions.

Nakano et al (5) analysed the non-linear convective diffusion equations one gets when constant pressure is assumed instead of constant permeate flux. Taking into account the osmotic pressure ($B \geq 0$) and assuming the membrane to be impermeable to solute ($R=1$) they solved the problem by using a series expansion of the differential equation which were treated numerically by Runge-Kutta technique. In the case when $B=0$ the results agree with Dresner results but when $B \neq 0$ the series solution breaks down at low value of time. They did therefore also apply an integral method in which the concentration profile was approximated as a cubic polynomial in η/a where $a(\tau)$ is the time-varying thickness of the concentration boundary layer. They improved the results of the integral method by treating them as zeroth approximation in an iterative technique.

Liu and Williams (4) performed a similar analysis but in this case the membrane was taken to be non-ideal ($0 < R \leq 1$). Their result was

$$C = \begin{cases} C_0 + (C_w - C_0) (1 - \eta/a)^3 & \eta \leq a \\ C_0 & \eta > a \end{cases} \quad (16)$$

William (6) used a perturbation technique to study the limiting case when $1-B \ll R$, $R=1$. Liu and Williams extended his results to account for all values of R , yielding

$$\frac{C}{C_0} = 1 + \frac{1-RB}{RB} \left[\operatorname{erfc} \left(\frac{\eta'}{2\sqrt{\tau''}} \right) - e^{\eta' + \tau''} \operatorname{erfc} \left(\frac{\eta'}{2\sqrt{\tau''}} + \sqrt{\tau''} \right) \right] \quad (17)$$

$$\text{where } \eta' = \eta R \quad \text{and} \quad \tau'' = \tau R^2 \quad (18)$$

Using an iterative approach they were also able to get an asymptotic solution for the case when $\tau'' \rightarrow \infty$, η fixed and $R=1$. Liu and William (4) extended this analysis to account for $R > 1-B$.

As mentioned by Liu and William (4) all these analyses mentioned above show good agreement with experimental data for certain range of time. But there is an intermediate range of time where these theories don't agree better than 10% with experiments.

Bellucio and Pozzy (7) tried to solve this problem both with an exact numerical solution and approximate analysis. These two analyses show good agreement. Comparisons of the numerical solution with experiments show good agreement even for the intermediate range of time.

(ii) Laminar flow systems. In comparison to the unstirred batch cell system theoretical treatment of flow systems are much more complicated because of the velocity profile that must be taken into account. This means that the equation of motion must be solved. In laminar reverse osmosis systems both the velocity

and the concentration boundary layers are developing in the entrance region of the feed channel (Fig. 2).

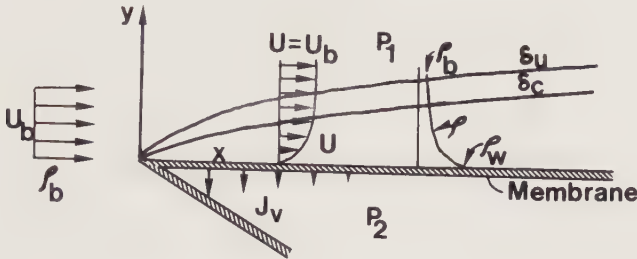


Fig. 2. Development of momentum and concentration boundary layers along the surface in membrane filtration.

As the molecular diffusion is slow, the concentration boundary layer is much thinner than the velocity boundary layer. But if the membrane channel is long enough both gradients will fill it completely. Thus there are two different regimes, the entrance region where the concentration gradient is increasing as the fluid moves downwards and the downstream region where the gradient extends over the entire channel.

Dresner (2) analyzed the laminar flow between parallel plates. He assumed the permeate flux to be constant which linearizes the problem. The velocity profile was taken to be fully developed at the channel inlet and complete rejection of solute was assumed. By using Leveque simplification for the velocity profile Dresner obtained an approximate closed form solution for the concentration polarization modulus C_w/C_b .

For the entrance region the solution were:

$$\frac{C_w}{C_b} = 1 + 1.536 \zeta^{1/3} \quad \zeta \leq 0.02 \quad (19)$$

$$\frac{C_w}{C_b} = 1 + \zeta + 5 (1 - \exp(-\sqrt{\zeta/3})) \quad \zeta > 0.02 \quad (20)$$

where

$$\zeta = \frac{J_v^3 h \cdot L}{3 U_0 D^2} \quad (21)$$

and for the downstream region

$$\frac{C_w}{C_b} = 1 + \frac{J_v^2 h^2}{3 D^2} \quad (22)$$

Equation 20 was extended by Gill et al (8) to account for laminar tube flow systems.

Sherwood et al (9) analysed the same system as Dresner using Graetz-type of analysis. Their solution agreed very well with an exact numerical solution. Fisher et al (12) extended this work to laminar flow in tubes. This system was also analysed by Gill et al (10) but with variable permeate flux (nonlinear wall boundary conditions). The results, obtained by using perturbation series solution, are valid for short distances from the channel inlet. Brian (11) solved this problem numerically and his results agree well with the solution of Gill et al (10). A great number of analysis of flow between parallel plates have been done by number of other investigators like Sourirajan (13), Hendricks and Williams (14), Doshi et al (15), Srinivasan and Tien (16, 39), Liu (18, 19), Dresner (20), and Bellucci and Esposito (21). Sourirajan (13), Dresner (20) and Srinivasan and Tien (22) did also analyse laminar flow inside tubes. This geometry has also been studied by several others investigators like Bansal et al (23), Tsao (24), Wino-grad et al (25) and Rao and Sirkas (26). First to analyse hollow fiber reverse osmosis systems were Hermans (27) and Gill and Bansal (28-30). Later Danavati et al (31), Doshi et al (32) and Vinayak et al (33) have improved these analyses.

It has been pointed out that high concentrations of solute at the membrane surface in laminar flow systems could create significant density differences between the bulk solution and the boundary layer. This could cause a secondary free convective flow because of the buoyancy effects. Ramanadhan and Gill (34) treated this problem analytically. Their result indicate that free convection can have significant influence on the velocity profile. Hendricks et al (35) and Johnson (36) have experimentally confirmed that free convection due to buoyancy effects exists. Derzansky and Gill (37) analysed the buoyancy effect in laminar horizontal tube flow. By assuming the mass transfer in boundary layer to be of Leveque type they found out that for the downstream region (about 16 diameters) both free and forced convection control the system behaviour. In their results correlations for Sherwood number in terms of Rayleigh number were obtained.

$$Sh = 0.434 Ra^{1/4} \quad Re \approx 540 \quad (23)$$

$$Sh = 0.485 Ra^{1/4} \quad Re > 980 \quad (24)$$

Chang and Guin (38) studied the same system as Derzansky and Gill. Their result was that when the product of the dimensionless permeation velocity (v_w) and

Rayleigh number exceeds about 7×10^3 free transport becomes a significant transport mechanism. Correlations for asymptotic Sherwood number Sh_∞ and the pseudo effective transition length Z_{tr} (the length at which free convection begins to have effect on the reverse osmosis process) were presented as

$$Sh_\infty = 1.09 (v_w Ra)^{0.166} \quad (25)$$

$$Z_{tr}^{1/3} = 1.19 (v_w Ra)^{-0.166} \quad (26)$$

$$\text{for } v_w Ra > 7 \times 10^3$$

Srinivasan and Tien (39) studied the connection between concentration polarization and the salt rejection parameter (R). By using integral approximation and numerical analysis an existence of maximum concentration polarization corresponding to a particular value of salt rejection ratio was confirmed. The precise value of rejection parameter R at which the maximum concentration polarization occurs varies with the axial distance. To be able to predict the presence and conditions for the occurrence of maximum concentration polarization they used a one-dimensional model to analyse the problem. In the analytical solution presented, two parameters exist that are determined by the membrane characteristics and the operating variables. By making a diagram where these two parameters are the axes they were able to draw curves that give those critical value of R which results in the presence of maximum wall concentration.

(iii) Turbulent flow systems. When the flow is turbulent the velocity distribution in the fluid is rather complex. The so called Nernst film model is very convenient and useful in solving the mass transfer problem for this kind of flow Sherwood et al (9, 40) and Brian (41). According to this model a very thin laminar film exists at the membrane surface (Fig. 3). The bulk flow outside the laminar film is turbulent and has uniform concentration. Concentration gradient does therefore only exist in the laminar film which accounts for all the resistance to mass transfer. Other assumptions that are made in this model is that the axial convection is neglected while the mass transfer perpendicular to the membrane surface occurs mainly by convection and diffusion. The permeate flux is taken to be constant and any curvature effects are neglected because Schmidt's number and Reynolds number are very high so the film thickness is small compared to radius of curvature.

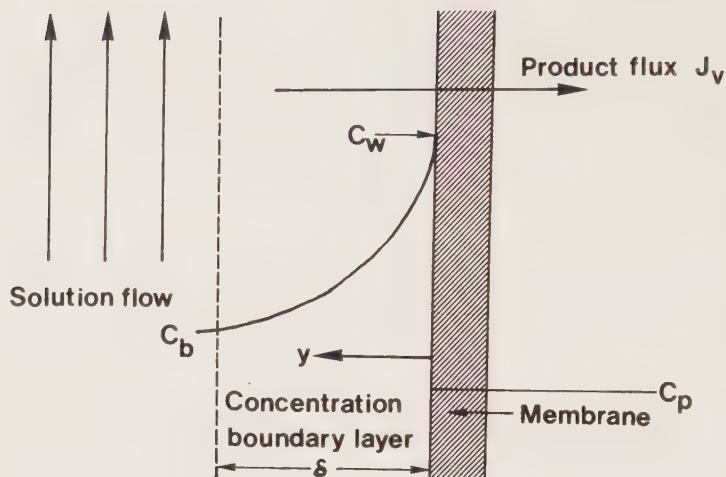


Fig. 3. Concentration profile for a RO-membrane.

If the membrane is assumed to be ideally semipermeable, that is completely impermeable to solute, the mass balance for the solute at steady state can be written as

$$J_v C = D \frac{dC}{dy} \quad (27)$$

This means that the flow of solute to the membrane surface by convection is counterbalanced by the diffusive flow back to the bulk solution. Integration over boundary layer δ gives

$$\frac{C_w}{C_b} = \exp \left(\frac{J_v \delta}{D} \right) \quad (28)$$

Because the film thickness δ is unknown one can instead use the mass transfer coefficient (k) defined as

$$k = D/\delta \quad (29)$$

Substituting this expressions into equation 26 gives

$$\frac{C_w}{C_b} = \exp \frac{J_v}{k} \quad (30)$$

This definition of k is valid if no flow exist through the channel wall but in this case it is assumed that the mass transfer coefficient is unaffected by the relatively low permeate flux found in reverse osmosis processes. Correlations of

the mass transfer coefficient for different channel geometries are available in the literature. It is often convenient to use the Chilton-Colburn J-factor which is related to k according to the equation

$$J = \frac{k \cdot Sc^{2/3}}{U_b} \quad (31)$$

For turbulent flow in many different channel geometries (no eddy diffusion) the Chilton-Colburn factor can be given with the use of empirical correlations such as

$$J = f/2 \quad (32)$$

where f is the Fanning friction factor.

Substitution of equation 29 and 30 into equation 28 gives

$$\frac{C_w}{C_b} = \exp \frac{2 J_v Sc^{2/3}}{f \cdot U_b} \quad (33)$$

The Fanning friction factor f can be given according to Blasius correlation (1) as a function of Reynolds number

$$f = 0.08 Re^{-1/4} \quad (34)$$

or according to other available correlations (42).

If the membrane is not ideally semipermeable ($R < 1$) the transmembrane flux of solute must be included in the mass-balance equation for the boundary layer. In that case equation 27 becomes

$$D \cdot \frac{dC}{dy} + J_v C - J_v C_w (1-R) = 0 \quad (35)$$

Integration gives

$$\frac{C_w}{C_b} = \frac{\exp \left(\frac{J_v \delta}{D} \right)}{R + (1-R) \exp \left(\frac{J_v \delta}{D} \right)} \quad (36)$$

Substituting equation 29 and 30 into equation 34 yields

$$\frac{C_w}{C_b} = \frac{\exp(2 J_v Sc^{2/3}/f U_b)}{R + (1-R) \exp(2 J_v Sc^{2/3}/f U_b)} \quad (37)$$

The film theory includes some simplifications known to be wrong like for instance that the eddy diffusion is zero within the boundary layer. Gill et al (8) made an analysis taking the eddy diffusion into account. By using the expression of Gill and Scher (43) for the eddy diffusivity they finally got the equation

$$\frac{C_w}{C_b} = \frac{\exp\left[\frac{\pi J_w Sc^{0.75}}{2 n, f^{0.5} U_b}\right]}{R + (1-R) \exp\left[\frac{\pi J_w Sc^{0.75}}{2 n, f^{0.5} U_b}\right]} \quad (38)$$

This equation gives essentially the same results as equation 35 except at low Reynolds number. Thomas (75) also developed an analytical solution where an eddy diffusivity term was included. Comparison with experimental result showed good agreement.

2.1.2 Ultrafiltration systems

In ultrafiltration processes the occurrence of concentration polarization is for the same reason as in reverse osmosis. The mechanism of mass transfer is governed by the same principles so the basic equations used to solve the problem are the same. But in ultrafiltration processes it is in the first hand macromolecules that are concentrated which means that another important factor must be taken in account, the characteristic of concentrated macrosolutes.

The properties of macromolecular solutions that are most important in this case are:

1. High concentration dependent viscosity
2. Low and concentration dependent self-diffusivity
3. They present low osmotic pressure
4. Gel can be formed at high concentration.

To day the most widely accepted model is the gel-polarization model which is based on the film theory principles (Fig. 4).

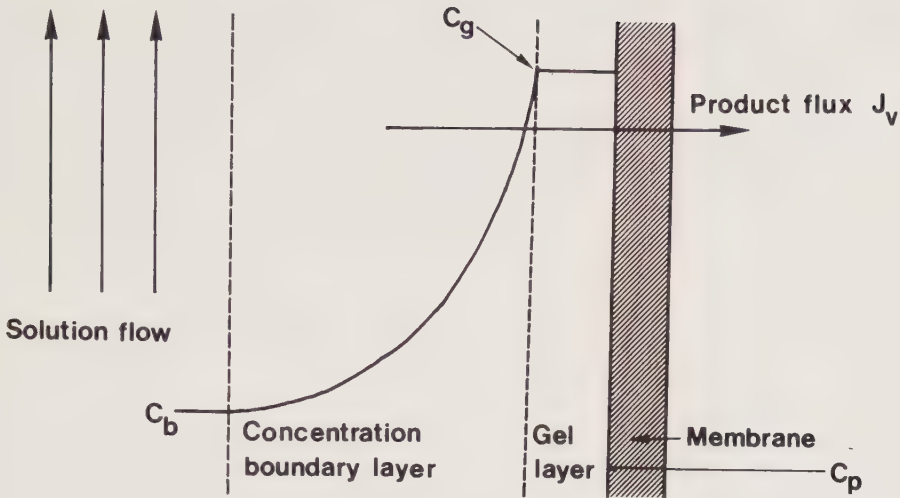


Fig. 4. Concentration profile for a gel-polarized UF-membrane.

This gel-polarization model is divided into two regions:

1. Where the concentration polarization modulus C_w/C_b is low enough so that the wall-concentration is lower than the gel-concentration.
2. Where C_w/C_b is large enough so that the wall concentration is equal to the gel concentration C_g .

In the first region the analysis is similar to the film theory for reverse osmosis which gave

$$J_v = \frac{D}{\delta} \ln \frac{C_w}{C_b} = k \ln \frac{C_w}{C_b} \quad (39)$$

In the second region the wall-concentration has reached the limiting gel concentration which is the highest concentration possible. All further build-up of solute must occur by thickening of the gel layer at the membrane surface. This leads to an increased resistance which reduces the transmembrane flux until the convective mass transfer of macrosolute to the membrane surface is counterbalanced by the diffusive transport back to the bulk solution. This means that when the wall concentration has reached the gel concentration the permeate flux at steady state is constant for given bulk concentration and mass transfer coefficient which can be seen by substituting C_g in equation 37 instead of C_w

$$J_v = k \ln \frac{C_g}{C_b} \quad (40)$$

In other words the permeate flux is entirely controlled by rate of back-transport from the surface into the bulk solution.

This means that any factor that increases the permeate flux without increasing the back-transport has no influence on the transmembrane flux at steady state condition. This explains why the flux, which initially increases linearly with the pressure, becomes independent of pressure as it increases.

In order to evaluate the mass transfer coefficient the Leveque solution can be used if the flow is laminar and the concentration profile is developing. For all thin-channel lengths of interest the Leveque solution gives (44).

$$Sh = \frac{k d_h}{D_s} = 1.62 (Re Sc \frac{d_h}{L})^{0.33} \quad (41)$$

where d_h is the equivalent hydraulic diameter

$$\text{or } k = 1.62 \left(\frac{u_b D^2}{d_h L} \right)^{1/3} \quad (42)$$

Substitution of this expression into equation 39 gives

$$J_v = 1.67 \left(\frac{u_b D^2}{d_h L} \right)^{0.33} \ln \frac{c_g}{c_b} \quad (43)$$

As can be seen from this equation the permeate flux increases with increasing velocity and decreasing channel height.

For turbulent flow in narrow channels the mass transfer coefficient can be given by the equation

$$Sh = \frac{k d_h}{D} = A Re^a Sc^b \quad (44)$$

where A, a and b are constants, determined experimentally.

This gel-polarization model was first presented by Michaels (45). In a very comprehensive study Blatt et al (46) confirmed the existence of pressure independent gel-polarized region. The qualitative agreement with experimental data are quite good but the quantitative predictions have been less satisfactory. Porter (44) discussed the differences that exist between the gel-polarization theory and experimental data. He tried to explain the large differences existing in ultrafiltration of colloidal suspensions with the so-called tubular pinch effect. This phenomenon is a shear-induced radial migration of colloidal particles which could possibly have a significant improvement on the back-transport from the membrane surface. Shen and Probstein (75) considered that the difference between theory and experiments could depend on variable transport properties of the macromolecular solution normal to the membrane surface in the concentration boundary layer. In the theoretical analysis accounts were made for diffusivity and viscosity dependences on concentration. The results were that the concentration de-

pendence of viscosity has little effect on the limiting flux but the diffusivity dependency of the concentration could not be ignored. Probstein et al (76) found out by means of an integral method that the appropriate diffusivity defining the flux in the gel-polarized region was found to be that at the gelling concentration, rather than at the bulk concentration. This means that the diffusivity coefficient evaluated at the bulk concentration in equation 40 should be replaced by one evaluated at the gel concentration to give

$$J_v = 1.62 \left(\frac{U_b D_g^2}{d_n \cdot L} \right)^{1/3} \cdot \ln \frac{C_g}{C_b} \quad (45)$$

Comparison of the analytical result with experimental data shows good agreement. Trettin and Doshi (47) claimed that the disagreements between theory and experiments are due to inaccuracy in the film theory. They used instead an integral method to solve the mass balance equation

$$U \frac{dC}{dx} + V \frac{dC}{dy} = \frac{d}{dy} \left(D \frac{dC}{dy} \right) \quad (46)$$

Assuming linear axial velocity and second order polynomial concentration profile they finally got a closed form solution expressed in dimensionless variables of the form

$$V_w = \frac{F_g^{-1}}{F_g} \left[K F_g \right]^{1/2} \cdot (\bar{D}_g)^{2/3} \quad (47)$$

where

$$V_w = |J_v|_L \left(\frac{D_b a}{3x} \right)^{-1/3} \quad (48)$$

F_g = Concentration polarization modules C_g/C_b

$$\bar{D}_g = \frac{D_g}{D_b} \quad (49)$$

$$a = \frac{3 U_b}{h} \quad (50)$$

$$K = 2 n^2 / (n+1) (n+2) \quad n = f(F_g) \quad (51)$$

This equation is identical with the equation developed by Probstein et al (76) when $n=2$, $K=2/3$.

Agreement between equation 45 and the exact numerical analysis of the mass balance equation 46 show less than 1% error. No comparison with experimental data was done. They compared in a flux versus C_g/C_b diagram the gel-polarization model with the exact solution at constant fluid properties. This comparison shows that for $C_g/C_b < 4$ the agreement is quite good while for $C_g/C_b > 4$ (that is lower bulk concentration) the exact solution gives higher flux. As a consequence they point out that if the gel-polarization theory is used to determine the gel-concentration by extrapolation very high potential errors can arise when the bulk concentration is low (C_g/C_b is high). They recommend therefore that if this method is to be used, C_g/C_b should be lower than 4. Whenever it is possible an independent method for determination of C_g should be used.

Kozinski and Lightfoot (48) analysed the two dimensional stagnation flow about a permeable rotating disk. Unlike the gel-polarization theory the osmotic pressure in ultrafiltration of macromolecular solutions was shown to be important factor in the ultrafiltration model. The effect of osmotic pressure in ultrafiltration processes was also pointed out by Goldsmith (49) and Carter and Newick (50). Déjmeš (51) presented an experimental method based on step changes in pressure which can be used to determine the relative influence of osmotic pressure and hydraulic resistance in ultrafiltration. His results for ultrafiltration of albumin indicate that the hydraulic model (gel-polarization theory) is correct.

Despite the fact that the qualitative agreement of the gel-polarization model with experimental data are good, there are some things observed in experiments that are not predicted by the theory. Most common observations are:

1. Slow decline of permeate flux with time
2. Reduction in feed solution-concentration is not followed by increase in permeate flux
3. Permeability loss due to macrosolute polarization or fouling is not restored in spite of chemical cleaning
4. Changes in solute-rejection behaviour of ultrafiltration membranes exposed to macrosolute solutions.

All these deviations show that lot of questions remains unanswered concerning the solid-liquid interface phenomena.

2.2 MEASUREMENTS OF CONCENTRATION POLARIZATION

In a great number of experiments the influence of concentration polarization have been observed, mostly in form of decrease in transmembrane flux and changes in rejection characteristics. As mentioned earlier lot of theoretical analysis have been done in order to get a model that describes this phenomena and predicts the transmembrane flux. The number of direct or indirect studies of this phenomenon to test the validity of these models are limited. Liu and Williams (4) used

electrical conductivity microprobes for measuring pointwise the salt concentration in an unstirred batch cell. Comparison with theories showed good agreement. Hendricks and Williams (14) measured the concentration profile for laminar flow in a thin channel between parallel plates with the same technique. By using probes with smaller diameter they were able to measure the concentration gradient down to 20 μm from the membrane. For Reynolds number higher than 1600 the diffusional boundary layer were too thin to be measured with this technique. They got reasonable agreement between theoretical and experimental values. Goldsmith and Lolachi (52) measured the concentration profile in a batch cell and in an annulus by using Ag-AgCl electrodes that respond to chloride ions in a Nernstian fashion. The agreement between theory and experiments were good for the unstirred batch cell and the entrance region of the annulus, where in the latter case comparison were done with theories for flat plates and tubes. For the downstream region the experimental results for the annulus were considerably lower than the values calculated for flat plates but compared to the theoretical values for the tubular geometry they showed good agreement. Welinder (53) used a holographic interferometry to measure the concentration polarization in an unstirred batch cell for several different solutes. Johnson (36) measured the concentration profile in a reverse osmosis system under natural convection by using interferometer with a helium-neon laser as a light source. His results agreed well with the mathematical model developed by Johnson and Acrivos (54). The main limitation of the interferometric technique is that a significant error may be introduced when measuring large concentration gradients, due to deflection of the light beam. Mahlab et al (142, 143) also used interferometry to measure the salt concentration gradient in an unstirred batch cell. They pointed out that even at very dilute feed concentrations the ray bending effects could severely effect the accuracy of the results. A theoretical analysis of the ray tracing of the deflected beam was presented and used to analyze the data.

2.3 METHODS USED FOR REDUCING CONCENTRATION POLARIZATION

It has been pointed out that concentration polarization arises because of the convective transport of solute to the membrane surface. It is therefore important to increase the back transport of solute to the bulk solution by some means in order to be able to decrease this accumulation at the membrane surface. The most usual way of solving this problem is to construct the membrane module so that the feed solution flows tangentially over the membrane surface. The flow is either turbulent or high-shear stress laminar. The most common modul configurations used commercially are:

Tube: The membrane is on the inside of the tube and the feed solution recirculate at velocity high enough so turbulent flow arises.

Plates: The module is so constructed that the feed solution flows in a thin

channel between two parallel plates, where the membrane can be on one or both sides of the channel. In this case the flow is laminar.

Hollow fiber: This type of module consists of a bundle of very fine tubes made out of the membrane material only and needs no supports. The active side can be either on the inside or outside of the tubes.

Spiral-wound: This module is made out of a plate of porous support material with membrane on each side. This plate is attached to a central tube and wound around it together with spacers to keep a suitable distance between the membranes. The feed solution flows axially along the wound cylinder while the permeate flows in spiral to the central tube.

During the last years some simple modifications of these traditional modules have been made like leaf design of the plates or construction of a spiral-wound module where the feed solution flows tangentially in spiral to the central tube.

Another type of modification is achieved by inserting different kinds of subjects in the feed channels which are meant to work as turbulent promoters. An example of these are static mixers, spiral wires and fluidized beds. The main aim of these turbulent promoters is to decrease the energy demand in membrane operation by forcing the flow towards the membrane surface and thus attain the same effective mass transport at lower circulation velocities. Experiments have shown that compared to empty feed channels turbulent promoters often give higher permeate flux for the same feed velocity (46, 55-63). It is not quite certain whether this is caused by decrease in fouling due to removal of the deposit from the membrane surface or it is caused by reduction of the concentration boundary layer. In order to destroy the concentration boundary layer Shaw et al (64) used a module where the membrane was replaced in some places with a non-rejecting sections, which increased the productivity and decreased product salinity. Kennedy et al (66, 67) showed that mass transfer coefficient in reverse osmosis could be increased significantly by pulsing the feed flow over the membrane. Thayer et al (68) used a different technique. They swept the membrane surface at a certain frequency by a back and forth movement of the feed liquid. Compared with the results obtained with the stirrer system the value of the mass transfer coefficient increased by a factor larger than three. Improvement in separation performance were also observed.

Different types of modules have been developed recently which are based on the principle that the membrane itself or a surface parallel to the membrane is rotating. In this way one can achieve flow conditions that are independent of the feed flow through the module. One of these rotating modules is made out of a pair of concentric cylinders where the inner one is rotating and carries the semipermeable membrane. Under certain circumstances a so-called Taylor vortex flow can be formed in the annulus which means that beside the primary high-shear stress flow a secondary flow exists, consisting of regular toroidal vortices rotating inside the annulus, which can improve the mass transfer considerably. Lopez (65) has claimed,

in his newly published thesis, that under certain conditions this module can completely eliminate both the macromolecular gel layer and the concentration boundary layer.

2.4 EFFORTS TO MAKE USE OF CONCENTRATION POLARIZATION

So far the problem of concentration polarization has been treated with methods that increase the transport of the rejected solute away from the membrane surface back to the bulk solution, thus dilute the highly concentrated solute which often is the final aim of the process. This has raised the question whether it is possible to separate this highly concentrated product from the bulk solution. Lee and Lightfoot (69) wondered if it were possible to skim off the boundary layer. They treated the problem theoretically and obtained very promising results. All practical experiments we know of (65, 70) have though not been as successful as one had hoped. This depends mostly on technical difficulties associated with the design and construction of such a module.

Another interesting way of making use of concentration polarization is in connection with the enzyme immobilization techniques (71-74). In this case the formation of gel on the membrane surface due to concentration polarization has been used as a basis for simple enzyme immobilization technique. Three different possibilities exist:

1. Only enzyme is in the feed solution so the gel formed is made of pure enzyme.
2. The feed solution contains both enzymes and inert proteins in excess so the enzyme is cogelified with the inert protein.
3. The enzyme is co-crosslinked to the inert protein before it is gelified.

Methods 2 and 3 have the advantage that gel concentration at the membrane surface is reached at lower enzyme concentration which means that less amount of the often expensive enzyme is needed. Compared to soluble enzyme systems this immobilized system has many advantages beside the application to continuous processes. Problems like enzyme inhibition by products, separation of enzyme from substrate and product and purification can easily be solved by this immobilization technique. Further advantages could be obtained when the substrate is very diluted and the membrane has high rejection against the substrate but is fully permeable to the product. In this case the enzyme is working at substrate concentration levels much higher than in the feed solution due to concentration polarization with simultaneous separation of substrate and product. Some negative effects can though arise in this immobilized system compared to the soluble enzyme system. It is not certain that the enzyme activity is the same when the enzyme is gelified as when it is free. The activity can even depend on the way the gel is formed. Another problem can arise if a concentration profile is formed within the gel layer which is lower than the feed substrate concentration level.

3. FOULING

3.1 DIFFERENT KINDS OF FOULANTS

Initially fouling was mostly described as a phenomenon that had a negative effect on the permeate flux of membrane processes as presented by Fenton-May (78) and Wiley et al (79) regarding pulp and paper effluent treatment and by Peri and Dunkely (80), Peri and Pompei (81) for whey and milk filtration respectively.

Dejmek (51) reviewed fouling in general, while Sammon and Stringer (82) and Belfort (83) reviewed fouling in water treatment.

The analysis of the foulant is often quite rough and mostly characterises it according to which group of compounds it belongs rather than giving its exact composition.

In table 3.1 such cases are listed.

A more detailed approach to reveal more about fouling was taken by Lee and Merson (104). They made scanning electron microscope studies of the fouling constituents of cottage cheese whey. γ -globulin formed granules that turned into a porous matrix. β -lactoglobulin and bovine serum albumin (BSA) both formed sheets or stands. α -lactalbumin formed smooth spherical particles. Permeation studies indicated the β -lactoglobulin and γ -globulin caused most of the fouling. Lee (105) and Hickey (106) also concluded that β -lactoglobulin was of major importance. They could however not deduce the fouling to a certain mechanism.

This was the first in a series of articles published by Lee et al that were concerned with the single constituents of the feed, how they corresponded to changes in the chemical environment and influenced the permeate flux - an approach also taken by others.

3.2 FACTORS INFLUENCING FOULING TENDENCY

3.2.1 Examples of interactions between solute and membrane

The previous examples have mostly illustrated efforts to identify what has accumulated on the membrane surface, without giving any hints of whether it is a general or specific accumulation, whether it is a rough poreblocking or a selective process. There is also the question whether the fouling process is a one step or a multi step process.

The interactions that might be responsible for fouling may be of purely chemical nature. It is then a question of hydrolysis of the membrane material (Kesting, 107) which is a well known problem with cellulose acetate membranes. It can also involve a chemical reaction between a solute and the membrane as described by Jonsson (108) for a case of sulphite liquors showing a severe flux decline. Substituted phenols are suggested to be the reason.

TABLE 3.1

Descriptions of fouling phenomena and foulants.

Foulant	Source	Author
Heavy metal oxides bacterial slimes CaSO_4 CaCO_3 Organic and inorganic colloids		Leiserson (84)
Iron	water, sewage treatment including iron coagulation	Kuiper et al (85) Cruver and Musbaum (86) McCutchan and Johnson (87) Grover and Delve (88)
Corrosion products	stainless steel test loop	Carter et al (89) Agrawal et al (90)
Microbial slime	waste water from sulfite pulp of wood	Wiley et al (79)
	aluminum treated sand filtered primary effluent	Feuerstein et al (91)
CaSO_4	sulfuric acid, pH-adjusted primary sewage	Feuerstein (92)
	polluted surface waters	Beckman et al (93)
Casein	whey	Lim et al (94)
Polyhydroxy aromatics	waste water	Cruver and Nusbaum (86)
Organic acids and polysaccharides	polluted surface water	Beckman et al (93)
Protein	milk	Glover and Brooke (95)
Organic material	simulated brackish water	Minturn (96)
Organics	plating wastes	Bevege et al (97)
Calcium phosphate complex	whey	Hayes et al (98)
Ca, P, organic material	trickling filter effluent	Bashow et al (99)
Pectin and insoluble cellulose-like material	mandarin juice	Watanabe et al (100)
Dissolved organic material	secondary sewage effluent	Winfield (101)
Oil	oily bilge water	Jackson et al (102) Bhattacharyya et al (103)
Calcium salt and humic acid	surface water and sewage	Sammon and Stringer (82)

Purely physical interactions occur by way of compaction - a mechanical effect.

However, most of the problems that are encountered in membrane filtration have physico-chemical reasons (Kesting, 107). They stem from differences in distribution of electrons in the atoms or molecules in the solute - membrane system. This gives possibilities to formation of a number of different types of bonds like ion-ion, ion-dipole and dipole-dipole bonds. Hydrogen bonds are of the last type (Deanin, 109). Michaels et al (110) found that small amounts of poly-vinyl methyl ether in the feed could increase the salt retention with only a small accompanying flux decline. Busby and Ingham (111) noticed that small amounts of plasma proteins enhanced the retention of poly ethylene glycol. The reason is believed to be solute - membrane interactions as the protein covers the membrane, a case often met in food processing.

In trying to reveal what kind of interaction that takes place - specific or nonspecific - tests have lead to the conclusion that specific sites are involved in "nucleation" followed by one or more additional steps.

Palmer et al (112) used CA-membranes in ultrafiltration of a solution containing, nonionic, anionic, cationic surfactants and other nonionic solutes. They concluded that specific solute-membrane interactions occur at low solute concentrations.

Hopfenberg et al (113) performed similar tests with various surfactants and other nonionic solutes. They concluded that factors like ion characteristics, surface activity of solute molecule and surface charge of the membranes are important for the existence and magnitude of fouling.

Pristoupil et al (114) described the formation of immobilized protein films on PVC-membranes and conclude that they are probably immobilized by short-range interactions with numerous $\text{CH}_2 - \text{CHCl}$ -groupings. The proteins do not become fully uncoiled.

Jackson (102) found that a nucleation - growth mechanism controlled the membrane fouling. The nucleation was performed by small colloidal ionhydroxide particles, faster the smaller the particle size or with increasing permeate flux. The pH influences the particle size: Near the isoelectric point coagulation takes place thereby forming too large particles to be attached to the membrane thereby diminishing nucleation sites and growth.

Bhattacharyya et al (103) describe fouling of non-cellulose acetate membranes by oily bilge water, synthetic lubricating oil and nonionic detergent in distilled water. The detergent-water system caused reversible detergent-membrane interactions causing flux lowering. In the system also containing oil a surface fouling results.

Winters and Isquith (115) reported that microfouling in some cases is a result of a sequence of events. 1. Chemical condition of the surface by rapid

absorption of large molecular weight substances, and concentration of low molecular weight substances. 2. Attachment and colonization by bacteria. 3. Colonization by other microorganisms. 4. Accumulation of debris, detritus and inorganic particles. The adhesion-inducing polymeric material is a glycoprotein polymer which is active in exceedingly low concentration.

Ingham and Busby (111) could discriminate the permeate flux drop caused by protein adsorption from that caused by gel formation when continuously adding albumin to the feed solution. Below 0.01 mg/ml adsorption took place and above 0.1 mg/ml gel formation started.

Howell et al (116) describe an ultrafiltration process as a three stage process with distinct time constants. The first lasts less than five seconds. A quasi-steady state concentration profile is reached at the interface. The second stage, one to ten minutes, solute adsorption on the membrane surface occurs. The third stage is governed by a reaction mechanism which produces a surface gel.

The reviewed cases point at a number of important factors that form the fouling situation, like membrane properties, solute properties and processing parameters. They in turn are to varying degrees influenced by the salt concentration and pH of the bulk solution.

3.2.2 Membrane properties

Membranes of different composition respond in different ways to the same situation. For example Lee (105) investigated the monolayer moisture content - reflecting the hydrophobicity - of three membranes. However, no correlation between flux and monolayer moisture was found.

Eykamp (117), Lee (105) and many others have noticed that cellulose acetate-membranes are less prone to fouling than non-cellulose membranes at least when processing proteinaceous solutions. What might be the cause for this difference?

Membranes may differ in many aspects. Freeman (118) made electrokinetic experiments with an asymmetric UF-membrane and concluded that pore size, pore shape, pore frequency and zeta potential are important properties. According to Kaneko et al (119), zeta potential differs with solute, production temperature and solute concentration.

The information about pores also gives an idea about how large the true surface exposed to the solute is.

Freeman reveals that there are 50 Å wide tubules and 50 Å wide slots penetrating the interface and coalescing to 300 Å tubules. There should according to him be $125 \text{ pores}/\mu^2$ of the 50 Å pores.

Further important properties are surface tension, surface charge, surface potential, all of which can be driven from the actual composition of the

membrane.

Lee (105) describes the three membrane types he used in the following way. Polysulfone is characterised by diphenylen sulphone repeating units (Fig. 5).

The oxygen molecules of the $-SO_2$ have two unshared electrons to donate giving rise to strong hydrogen bonds to solvent or solute molecules.

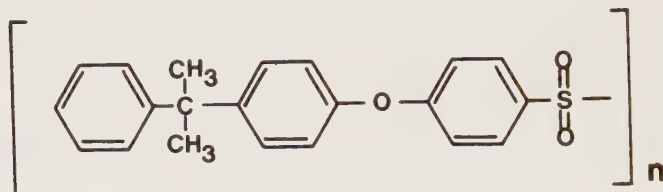


Fig. 5. The repeating unit of polysulphone.

Polyamide membranes contain repeating units of hydrocarbons linked by amide groups, $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{N} -$ (Fig. 6).

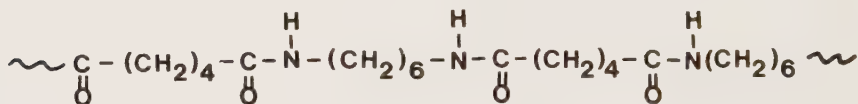


Fig. 6. A sequence of a polyamide material.

The amide bonds that are responsible for high surface energy and surface tension, cause polarity with possibility to form hydrogen bonds.

Cellulose acetate (CA) membranes consists of acetylated D-glucose units (Fig. 7).

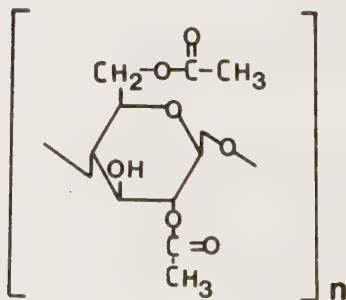


Fig. 7. The repeating unit of a cellulose acetate membrane.

The polarity - caused by an uneven distribution of electron clouds - is described by charge density, dipole moment and capacity to form hydrogen bonds. Interaction is expected to occur with polar species.

When interactions become appreciable the cohesive forces are modified by what is called a solubility factor, i.e. the chemical affinity of the species for the membrane.

3.2.3 Influence of salts

Salts may either influence 1) the solubility of the foulants, 2) interact with the membrane or 3) increase the osmotic pressure.

Hayes et al (98) studied the role of calcium in fouling. Sequestering with EDTA and pH adjustment of whey to pH 6.2 increased the permeate flux. However, a control sample did not justify any conclusion about the role of calcium.

Lee (105) states that it is likely that calcium up to a certain concentration may be directly involved in the stability of proteins, but at higher concentrations simply increases the ionic strength of the solution.

He also studied the role of the whey components phosphorus and leucin in fouling of UF-membranes. The results are rather inconclusive indicating the great complexity in dealing with natural systems containing solutes of different classes and comparing different membranes with each others. However, he showed that phosphorus plays an important role and that its binding is affected in different ways by the addition of Ca, lactose and β -lactoglobulin. Indications of multi-binding and of competition with phosphorus for binding to the membrane were seen.

Lee et al (120) studied the effect of calcium and EDTA addition to a whey solution. CaCl_2 and NaCl of similar ionic strength caused a thinning of the protein sheet, indicating the importance of ionic strength rather than the possibility of specific actions by calcium. "Salting in" - increasing solubility due to the formation of an ionic sheath around the protein molecules, was believed to be the reason. Its opposite "salting out" occurs at high ionic strength and decreases the solubility. EDTA reduced the size of the calcium-caseinate complex. Too much removal produced thicker deposits.

Bevege (97), working with simulated surface water including humic acid, bentonite clay, divalent and trivalent ions in trace amounts, noticed interactions between clay - humic acid and humic acid - multivalent ions. One possible explanation is a destabilization of polyelectrolytes through neutralization with polyvalent cations. Another possibility is adsorption of the cations on humic acid.

3.2.4 Effect of pH and temperature on fouling

Muller et al (121) studied the permeation rate of UF of two kinds of whey under different pH conditions. Below pH 4.3-4.5 the rate was low but increased above pH = 4.5 for one of the wheys only.

Hayes et al (98) in their investigations of the influence of the calcium concentration also noticed a strong pH-dependence. The combined effect was considered to be a selective coagulation of casein.

The effect of pH in the fouling of a membrane is related to the degree of protein aggregation and to the mode of aggregation (Lee, 105). pH of a solution corresponds to a certain characteristic charge of the proteins. This in turn influences the ionic strength and thus the protein solubility. pH influences particle size. At the isoelectric point (zeta potential = 0) a low flux is observed in UF and RO. At this point large particles form and settle on the membrane. Jackson et al (102) observed the opposite when working with iron hydroxide.

In for example whey systems, but probably also in other natural systems, some constituents may act as flocculating agents, adsorb on membranes and bind polymers in the feed to the membrane.

Winfield (101) noticed that pH 6 gave higher fluxes than pH 5 and pH 7 in RO of secondary sewage effluents.

The denaturation of whey proteins by means of high temperature has been reported by Hayes (98) and Muller (121) to cause a flux increase in RO, but did not work well in UF. The mechanisms is thought to be aggregate forming, possibility between casein components and β -lactoglobulin.

Care has also to be taken to avoid the formation of apatites which is pH depending.

3.2.5 Effects shear stress and pressure

Parallel to looking at what causes the fouling it is natural to look at the effects of it and how it can be counteracted. Thomas et al (17), Kuiper et al (85) observed how the permeate flux drastically dropped as a result of fouling. Sometimes, the retention also changed. Kuiper saw a decrease which seems to be mostly common. Belfort (122) also observed a decrease in operating a protected RO membrane. An increase was noticed in a system filtering poly ethylene glycol after the addition a protein to the feed solution (111).

The flux decline due to fouling depends also on the initial flux showing a more severe decline with high initial flux than with low flux. This is predicted by Gutman (123). The feed velocity or rather shear stress over the membrane surface is of major importance (Jackson et al, 102, Minturn, 96, Hiddink et al, 124). In some cases a threshold velocity has to be superceded in order to avoid

drastic fouling (Kuiper, 85).

In general the effect of raised stress is positive. Hiddink et al (124) also show how the fouling in RO of skim milk depends on the applied pressure. Especially at higher pressures than 2.5 MPa the influence of fouling becomes important.

Some evidence suggests that high shear stress itself does not hinder the physico-chemical process of fouling (Lopez, 65) but it can diminish to a large extent the negative effects of it.

Madsen (125) has as an explanation to the higher fluxes than the theoretically calculated. He puts forward the theory of wave and vortex formation in a thin channel system. He also considers different pore models and concludes that a model based on a long-jump diffusion theory and oscillating pore openings give reasonable results. Gerndel (126) presented a study on deposit resistance and thickness in ultrafiltration of milk. He shows the dependence of deposit thickness on shear stress and bulk concentration.

3.3. MATHEMATICAL MODELLING OF FOULING

3.3.1 Model by Kimura and Nakao

Kimura and Nakao (127) based their model of fouling of CA tubular RO and UF membranes on a modification of the gel polarization model by Michaels (45).

$$J_v = k \ln \left(\frac{C_g}{C_b} \right) \quad (52)$$

It is extended to accumulation of a deposit under unsteady state.

$$J_v \cdot C_b - k C_b \ln \frac{C_g}{C_b} = \rho \frac{dl}{dt} \quad (53)$$

The resistance to flow consists of the membrane resistance R_m and the deposit resistance of the layer $a_1 \cdot l$.

$$J_v = \frac{p}{R_m + a_1 \cdot l} \quad (54)$$

Introduction of a dimensionless resistance $\left(\frac{R_{mo}}{R_m} \right) = (t)^{-m_1}$ and its time dependence and a dimensionless flux $f_1 = \frac{J_v}{J_{vo}}$ and writing eq 53 on dimensionless form yields equation 55 where t is the dimensionless time.

$$\frac{\theta_T}{f_1^2} \frac{df_1}{dt} + f_1 - r = - \theta_T m_1 (t)^{m_1 - 1} \quad (55)$$

$$\theta_T = \frac{\rho}{a_{T_0}} \frac{p}{J_{v0}^2 C_b} \quad (56)$$

θ_T expresses the time constant of the flux decline and r is expressed by eq. 57.

$$r = k \frac{\ln \frac{C_g}{C_b}}{J_{v0}} \quad (57)$$

Equation 55 can be solved numerically if m_1 , r and θ_T are given.

For ultrafiltration or low pressure reverse osmosis, the membrane compaction can be neglected ($m_1 = 0$) and eq. 55 can be integrated:

$$\ln \left[\frac{f_1 (1-r)}{f_1 - r} \right] - r \left(\frac{1}{f_1} - 1 \right) = \frac{r^2}{\theta_T} (t-1) \quad (58)$$

There is no indication on how well it fits with experimental results.

3.3.2 Model by Carter and Hoyland

Carter and Hoyland (128) describes the build up of rust fouling layers on RO-membranes in turbulent flow. The development of a transient fouling layer depends on the rates of deposition r_d and removal r_r of rust. E is the effective thickness of the layer.

$$\frac{dE}{dt} = r_d - r_r \quad (59)$$

Assuming that the removal depends directly on the shear τ_w at the surface gives

$$\frac{dE}{dt} = r_d - K_1 \cdot \tau_w \cdot E \quad (60)$$

K_1 = proportionality constant.

Integrating and exchanging τ_w according to the Blasius equation yields

$$\frac{E}{h} = K_3 \frac{r_d}{RE^{1.75}} \left[1 - \exp \left(- \frac{RE^{1.75}}{K_3 h} \cdot T \right) \right] \quad K_3 = \frac{16 h}{K_1 K_2 \rho v^2} \quad (61)$$

h = half channel height

RE = Reynolds number

The rate of build up and final thickness are strongly dependent on the shear stress at the membrane surface but insensitive to flux rate and ferric hydroxide concentration.

3.3.3 Model by Gutman

Gutman (123) remarks that neither of the two previous fouling models have found widespread acceptance. Instead he introduces a "turbulence burst model" for RO. The reentrainment of particles from a fouling layer is ascribed to turbulence bursts which sweep down into the laminar sublayer and remove a small part of it from the wall. This rate is found to occur at time intervals θ proportional to $100 \mu/\tau_w$.

The starting point is the nett rate of fouling

$$\frac{dm}{dt} = r_d - r_e \quad (62)$$

Carter did not count for any extra resistance due to the fouling layer but only for increased osmotic pressure. Gutman introduces a hydraulic resistance R_f proportional to the weight of the fouling layer.

He arrives at an integrated equation describing the flux decline of the membrane with time for the two cases where the fouled membrane flux is either smaller or larger than twice the mass transfer coefficient.

$$J_f < 2k_g$$

$$\frac{J_v}{J_f} = 1 + \frac{\alpha a_2}{A_1 \cdot U} \left[1 - \frac{\left\{ \frac{2 k_g/J_f + 1}{2 k_g/J_v + 1} \right\} - \frac{J_v A_1 \cdot U}{2 k_g (A_1 U + \alpha a_2)}}{\exp \left\{ - A_1 U \left[k_g + \frac{J_v A_1 \cdot U}{2 (A_1 U + \alpha a_2)} \right] t \right\}} \right] \quad (63)$$

$$J_f > 2 k_g$$

$$\frac{J_v}{J_f} = 1 + \frac{\alpha a_2}{A_1 \cdot U} \left[1 - \exp \left\{ - \frac{(J_v/J_f - 1 - J_v A_1 U t)}{1 + \alpha a_2 / A_1 U} \right\} \right] \quad (64)$$

Comparison with experimental data shows that according to the model the flux change with time depends upon the initial flux J_v , the concentration of the foulant in the feed (a) the feed velocity (U) the mass transfer coefficient k_g and the parameters α and A_1 .

The experimental initial fluxes do not agree well with the theoretical values, but final flux values are better predicted in processing of sewage water.

3.3.4 Model by Belfort and Marx

Belfort and Marx (122) have for the sake of easy comparison of membranes performance converted the standard filtration equation to a modified gel filtration equation which describes the accumulated flux of permeation coefficient as a function of accumulated permeation volume V and normalizes different membranes with respect to fouling and compaction.

$$\left(\frac{1}{S} \frac{dV}{d\theta} \right)^{-1} = \left(\frac{\mu \cdot \alpha_1 \cdot \omega}{\Delta p_c \cdot S} \right) V + \left(\frac{\mu r^1}{\Delta p - \sigma \Delta \pi} \right) (1 + \beta V^n) \quad (65)$$

$n = 1$ during the initial transient period

$n = 0$ during the steady state period

β = constant characteristic of the membrane

$\omega = w(\theta)$ for variable suspended feed concentration with θ

$W = w(0) = \omega_0$ for constant suspended feed concentration with θ

For the initial transient period ($n=1$), integrating the equation above and dividing by V .

$$\theta/V = k_5 \cdot V/2 + k_4 + k_6/V \quad (66)$$

In the later stage of the initial period

$$\theta/V = k_5 \cdot V/2 = k_4 \quad (67)$$

For the steady state period ($n=0$) after integration the equation becomes

$$\theta/V = k_3 V/2 + k_7 + k_8/V \quad (68)$$

Equation 67 and 68 should join smoothly as $V \rightarrow \infty$. The equation becomes

$$\theta/V = k_3 V/2 + k_4 (1+\beta) \quad (69)$$

which is analogous to the standard filtration equation.

The corresponding equations for exponentially decreasing suspended solids feed concentration are also given.

3.3.5 Model by Hiddink et al

Hiddink et al (124) give an idea of how large a part of the total flux decline that is due to fouling, concentration polarization and membrane resistance in RO of whey and skim milk. The flux that takes account of the osmotic pressure can be calculated from eq. 70

$$J_v = (\Delta p - \Delta \pi) / R_m \quad (70)$$

The pure water flux can also be calculated from this equation when $\Delta \pi = 0$. If also concentration polarization occurs the build up of solutes at the membrane surface can be described with the knowledge of physical properties of the lactose and the salts thus giving the mass transfer coefficients. Then it is possible to calculate the permeate flux according to eq. 71.

$$J_v = (\Delta p / R_m) - (\pi_{b1} / R_m) \exp(-J_v / k_1) - (\pi_{b2} / R_m) \exp(-J_v / k_2) \quad (71)$$

The fluxes calculated according to eq. 70 and 71 and experimental results can be visualized in a plot of permeate flux versus osmotic pressure. From such a plot the magnitude of fouling can be seen as the difference between the curve according to eq. 71 and experimental results.

3.4 METHODS FOR FOULING ANALYSIS

Fouling analysis requires techniques for identifying the deposits, for characterizing solutes and suspended materials and membranes.

The deposits on the membranes can be identified as for example in references 85-103. It is a matter of classifying the components of the deposit as organic or inorganic substances, metal or non-metal substances, proteins, fats or carbohydrates. Normally the deposits are present in large enough quantities to allow the use of macro analyses in determining for example Fe, Ca, organic acids, polysaccharides, P, etc.

Lee et al (104) used SDS-gel electrophoresis in identification of whey proteins in combination with scanning electron microscopy and permeation studies.

Jonsson et al (108) used mass spectrometry and gas chromatography when identifying aromatic compounds in the membrane.

Watanabe (100) used gel filtration and colorimetry when analysing pectin deposited on a membrane. The pectin layer was washed off the membrane prior to analysis.

Glover (95) analysed the structure of a deposit with transmission electron microscopy. Lee (105) used radio actively labelled phosphorus and leucine in ultrafiltration experiments. The counting took place in a liquid scintillation spectrometer. Kaneko (119) measured zetapotential under a reverse osmosis process. Similar electrokinetic experiments were performed by Freeman (118).

In an article by Baier (139) a number of experimental techniques are listed. They are MAIR, multiple attenuated reflection infrared spectroscopy, ellipsometry, critical surface tension determination and contact potential determination. MAIR and ellipsometry are optical methods which allows microscopic amounts of material to be analyzed regarding composition and thickness and refractive index respectively. The surface tension and contact potential determinations give further information about the solid surfaces that might prove useful in fouling studies.

3.5 METHODS TO DIMINISH OR PREVENT FOULING

3.5.1 Pretreatment of the feed solution

In table 3.2 pretreatment methods are listed.

TABLE 3.2
Pretreatment methods

Process	Product	Operation	Author
Heat treatment and pH adjustment	whey whey	UF RO	Hayes et al (98) Smith et al (129)
pH adjustment	whey whey	RO UF	Smith et al (129) Lee et al (120)
ion exchange	whey whey	RO UF	Smith et al (129) Hayes et al (98)
Ca-sequestering agents (EDTA)	whey	RO	Smith et al (129) Lee et al (120)
Glycerol addition to feed solution	polypeptide, enzyme	UF	Melling (130)
Change of ionic strength	whey	UF	Lee et al (120)
Modification of side chain (sulphydryl-, carboxyl-)	whey	UF	Lee et al (120)
Pre-ultrafiltration	whey	UF	Lee et al (131)

Many of the reasons behind the use of feed pretreatments have been explained in the previous chapters. The addition of glycerol (10 %) to the feed (130) has increased the flux - possibly by increased hydration of the membrane - and increased the retention of proteins. Modifications of side chains of for example BSA and β -lactoglobulin or carboxyl groups of β -lactoglobulin in order to prevent fouling showed some improvements but should be regarded as an example of chemical modification that could be performed if the additives involved were allowed. Lee et al (120) conclude that from a commercial point of view pH-change or EDTA-addition could be feasible.

Apart from the listed methods there exist in water treatment a large number of unit operations, which are parts of the purification, that also aim to change the feed; biological methods, adsorption methods, coagulation, filtration etc.

3.5.2 Change of membrane properties

In table 3.3 different ways of altering membrane properties are listed.

TABLE 3.3

Changes of membrane properties

Type of manipulation	Product	Process	Author
Charged membranes			
sulphonate polymer		UF	Gregor Gregor (132)
sulphonation, amination		RO	Nomura et al (133)
electrically polarized-electret membranes		RO	Wallace et al (134)
Immobilization of enzymes on the membrane surface	milk, raw sewage	UF	Wang et al (135)
	albumin, haemoglobin	UF	Howell et al (116)
Use of protective cover	colloidal particles	PO	Belfort et al (122)
fixed			
dynamic			
Use of small electric current			Spiegler (136)

The suggestion that the use of charged membranes as a means to at least partly prevent fouling has been put forward as a great future potential by Channabasappa (137). Immobilization of enzymes on membranes has proven to give higher fluxes than naked membranes. Wang et al (135) report a 90 % increase in UF of reconstituted milk during the 50 first processing hours and a 12 % increase when processing sewage water.

They also present a model for their enzyme-membrane that includes the growth of a gel layer and the kinetics of the enzyme. A fair agreement between calculation and experiment is shown. Belfort et al (122) suggests the use of a protective cover or top of a RO-membrane, either fixed (Millipore, Nuclepore membrane) or a dynamic precoat type protection. Increased fluxes and decreased rejection result.

A US patent by Spiegler (136) claims that use a small electric current 10-100 mA/cm² and a potential difference of 2-20 V has a positive action on the flux. The membrane serves as anode and the cathode is a metal electrode in the center of the tube.

3.5.3 Change in process conditions and optimization of flow conditions

In table 3.4 changes in process conditions and optimization of flow conditions are listed. Essentially, it is a question of changing the shear stress at the membrane surface.

TABLE 3.4
Changes in process conditions

Type of manipulation	Author
Altered linear velocity	Hiddink et al (124) Thomas et al (17) Kuiper et al (85)
Use of static mixers and displacement rods	Dejmek (51)
Use of beads in a fluidized bed	Hiddink et al (124)
Use of moving balls	Lowe et al (138)
Use of rotating membranes or rotating elements	Lopez (65)

Manipulations aiming at increased shear forces at the membrane surface has been used to diminish the deleterious effect of fouling as well as of concentration polarization. Recent developments are the rotary module, where either the membrane or a disc rotates; and the fluidized bed system.

The rotary module (65) has a potential application in processing highly viscous products in a single pass process, but has up till now a large energy demand. The action of the fluidizing beads (glass, 2-3 mm diameter) reported is either as turbulence promoters or eroding the surface gel layer (124).

3.5.4 Cleaning

Cleaning of membranes is performed in order to maintain a certain microbiological standard as well as to get rid of foulants. Belfort (83) has in a review listed techniques for cleaning of RO-membranes used in municipal waste water renovation. Many of the methods mentioned are also used in other cases. In for example the dairy industry the use of proteolytic enzymes in the detergent works well but in many other applications the disability to clean the membrane and to restore the flux is a large problem.

3.6. PARALLELS TO FOULING OF OTHER KINDS OF "PROCESS EQUIPMENT"

As fouling is not only encountered in membrane filtration but to at least some degree in all kinds of process equipment working with possible foulants, there are some parallels to draw and a possibility to collect further information about the reasons for fouling.

Baier (139) mentions adhesion in systems like blood tissue, oral and uterine cavities, saliva and sea water. In each of these a conditioning of the solid surface takes place before the adhesion of cellular material. The conditioner is predominantly proteinaceous. This new interface provides anchor points for strong bonding with muco-polysaccharides from cellular species at the surface.

The conditioners are considered to be reasonably specific. In the case of blood and a non-physiological interface, there are some evidence that the conditioner is fibrinogen, and in maritime environments and in the oral cavity it is a glycoprotein.

This information gives some hints about where to concentrate the studies of fouling of membranes.

Fouling can be regarded as an adsorption phenomenon on the one hand and as a transport phenomenon on the other. Thus more knowledge is needed about adsorption phenomenon with macromolecules like unfolding, orientation changes etc. For example Norde and Lyklema (140) describe protein adsorption on polystyrene surfaces from a thermodynamic point of view.

From the engineering point of view one has to realize that everything that happens takes place within the boundary layer and that the conditions are quite different there from those in the bulk fluid. The scale of reference is no longer mm or m but micrometers or Ångströms. Important driving forces within the boundary layer are normally neglected in engineering practice for example free surface energy gradient, wall potential gradient, streaming potential gradient as well as temperature gradient (Sandu, 141).

There are a number of analysis methods available for surface analysis (Baier, 139): multiple attenuated internal reflection spectroscopy ellipsometry, critical surface tension determination, contact potential determination

and others.

Till now membrane manufacturing has mostly aimed at producing high flux, chemically inert membranes. However, additional efforts may result in the creation of tailormade surfaces that are resistant to fouling even of complex solutions with the aid of methods and approaches like those mentioned above.

Symbols

A	= membrane constant, equation 4
A_1	= $\rho\beta/100 \mu$
a	= $3U_b/h$
a_1	= specific filtration resistance
a_2	= concentration of foulant
B	= $\pi_0/\Delta p$
C	= concentration of solute
D	= diffusivity coefficient
d_h	= equivalent hydrolic diameter
E	= effective thickness of the fouling layer
F_g	= C_w/C_b
f	= Fanning friction coefficient
f_1	= J_v/J_{v0}
$\vec{a}$	= gravitational acceleration
h	= half channel hight
J	= Chilton-Colburn factor
J_f	= permeation velocity of fouled membrane
J_v	= permeation velocity
$ J_v $	= absolute value of the permeation velocity
$ J_v _L$	= limiting permeation velocity
K	= constant, equation 51
K_1, K_2, K_3	= proportionality constants
K_4	= hydrolic resistance of fouling layer per unit mass
k	= mass transfer coefficient
k_1, k_2	= mass transfer coefficients for lactose and salt respectively
$k_3, k_4, k_5, k_6, k_7, k_8$	= constants
k_9	= liquid side mass transfer coefficient
L	= channel length
l	= thickness of deposit layer
m	= mass of foulant per unit area
m_1	= coefficient of membrane compaction
n, n_1	= constants
p	= applied pressure
Δp	= pressure drop across membrane
Δp_c	= pressure drop across the cake
R	= rejection coefficient
R_m	= membrane resistance
Ra	= Rayleigh number

Re	= Reynolds number
r	= $\frac{k \ln (C_g/C_b)}{J_{v0}}$
r'	= intrinsic membrane resistance
r_d	= rate of deposition
r_e	= rate of re-entrainment
r_r	= rate of removal
s	= exposed surface area for transport
Sc	= Schmidt number
Sh	= Sherwood number
t	= time
u	= axial velocity
V	= transverse velocity
V_1	= accumulated volumetric throughput
$\frac{V}{V}, \frac{V_w}{V}$	= dimensionless permeation velocities
$\frac{V}{V}$	= mass average velocity
$w(\theta)$	= turbidity of feed time θ
x	= axial distance coordinate
y	= transverse or radial coordinate
y_1	= transverse or radial distance from membrane surface

Greek letters

α	= K_4/R_m
α_1	= average specific cake resistance
β	= fraction of surface cleared by turbulence burst
β_1	= membrane constant, equation 63
δ	= boundary layer thickness
ζ	= parameter defined according to equation 21
η	= parameter defined according to equation 14
θ	= accumulated time
θ_T	= $\frac{\rho p}{a \tau_0 J_{v0}^2 C_b}$
μ	= dynamic viscosity
ν	= kinematic viscosity
π	= osmotic pressure
$\Delta\pi$	= osmotic pressure difference across membrane
$\pi_{b,}$	= osmotic pressure of lactose

π_{b2}	= osmotic pressure of salt
ρ	= fluid density
σ	= Staverman reflection coefficient
τ	= shear stress, time, (eq 53)

Subscripts

b	= bulk condition
g	= gel condition
o	= condition at channel inlet or zero time
p	= permeate condition
w	= membrane surface condition

Operators

$\vec{\nabla}$	= "nabla" operator
$\frac{D}{Dt}$	= substantial derivative

LITERATURE

- 1 R.B. Bird, W.E. Stewart and E.N. Lightfoot, Transport Phenomena, John Wiley & Sons, Inc. New York (1960).
- 2 L. Dresner, Boundary layer built-up in the demineralization of salt water by reverse osmosis, Oak Ridge Nat. Lab. Rept 3621 (1964).
- 3 R.J. Raridon, L. Dresner and K.A. Kraus, Desalination (1966) 210-224.
- 4 M.K. Liu and F.A. Williams, Int. J. Meat Mass Transfer 13 (1969) 1441-1456.
- 5 Y. Nakano, C. Tien and W.N. Gill, A.I.Ch.E.J. 13 (1967) 1092-1098.
- 6 F.A. Williams, Siam J. Appl. Math. 17 (1969) 59-73.
- 7 F. Bellucio and A. Pozzy, Int. J. Heat Mass Transfer 18 (1974) 945-951.
- 8 W.N. Gill, L.J. Derzansky and M.R. Doshi, Surface and Colloid Science IV, John Wiley & Sons, Inc. New York (1971) 261.
- 9 T.K. Sherwood, P.L.T. Brian and R.E. Fisher, M.I.T. Desalination Res. Lab. Rept 295-1 (1963).
- 10 W.N. Gill, C. Tien and D.W. Zeh, Ind. Eng. Chem. Fundam. 4 (1965) 433-439.
- 11 P.L.T. Brian, Ind. Eng. Chem. Fundam. 4 (1965) 439-445.
- 12 R.E. Fisher, T.K. Sherwood and P.L.T. Brian, M.I.T. Desalination Res. Lab. Rept 295-5 (1964).
- 13 S. Sourirajan, Reverse Osmosis, Logos Press Ltd, London (1970).
- 14 T.J. Hendricks and F.A. Williams, Desalination 9 (1971) 155-180.
- 15 M.R. Doshi, A.K. Dewan and W.N. Gill. A.I.Ch.E. Symp. Ser. 68 (1971) 323-339.
- 16 S. Srinivasan and C. Tien, Desalination 5 (1968) 139-156.
- 17 D.G. Thomas, Ind. Eng. Chem. Fundam. 12 No. 4 (1973) 396-405.
- 18 M.K. Liu, Desalination 9 (1971) 181-191.
- 19 M.K. Liu, Appl. Sci. Res. 26 (1972) 349-360.
- 20 L. Dresner, O.S.W. Res. Dev. Progr. Rept 897 (1973).
- 21 F. Bellucci and N. Esposito, Desalination 28 (1979) 181-191.
- 22 S. Srinivasan and C. Tien, Desalination 9 (1971) 127-139.
- 23 B. Bansal, R. Deluca, L. Derzansky, A.R. Dewan, M.R. Doshi and R.A. Shaw, O.S.W. Res. Dev. Progr. Rept 854 (1973).
- 24 C.K. Tsao, Desalination 8 (1970) 234-258.
- 25 Y. Winograd, M. Toren and A. Solan, Desalination 14 (1974) 173-187.
- 26 G.H. Rao and K.K. Sirkar, Desalination 27 (1978) 99-116.
- 27 J.J. Hermans, Membrane Digest 1, No. 3 (1972) 45.
- 28 B. Bansal, A theoretical and experimental study of hollow fiber reverse osmosis, Ph.D. thesis, Clarkson College of Technology, Postam (1973).

- 29 B. Bansal and W.N. Gill, A.I.Ch.E. Water Symposium (1974).
- 30 W.N. Gill and B. Bansal, A.I.Ch.E.J. 19, No. 4 (1973).
- 31 M.S. Danavati, M.R. Doshi and W.N. Gill, Chem. Eng. Sci. 30 (1975) 877.
- 32 M.R. Doshi, W.N. Gill and V.N. Kabadi, A.I.Ch.E.J. 23 (1977) 765.
- 33 N.K. Vinayak, M.R. Doshi and W.N. Gill, Chem. Eng. Commun. 3 (1979) 339-365.
- 34 K. Ramanadhan and W.N. Gill, A.I.Ch.E.J. 15 (1969) 872-884.
- 35 T.J. Hendricks, J.F. Macquin and F.A. Williams, Ind. Eng. Chem. Fundam. 11 (1972) 276-279.
- 36 R.A. Johnson, A.I.Ch.E.J. 20 (1974) 966-974.
- 37 L.J. Derzansky and W.N. Gill, A.I.Ch.E.J. 20 (1974) 751-761.
- 38 C.Y. Chang and J.A. Guin, A.I.Ch.E.J. 24 (1978) 1046-1054.
- 39 S. Srinivasan and C. Tien, Desalination 13 (1973) 287-301.
- 40 T.K. Sherwood, P.L.T. Brian, R.E. Fisher and L. Dresner, Ind. Eng. Chem. Fundam. 4 (1965) 113-118.
- 41 P.L.T. Brian, Desalination by Reverse Osmosis. U. Merten (ed.) M.I.T. Press, Cambridge, Mass. (1966) 161-202.
- 42 T.K. Sherwood, Chem. Eng. Progr. Symp. Ser. 55, No. 25 (1959) 71.
- 43 W.N. Gill and M. Scher, A.I.Ch.E.J. 7 (1961) 61.
- 44 M.C. Porter, Ind. Eng. Chem. Prod. Res. Develop. 11 (1972) 234-248.
- 45 A.S. Michaels, Chem. Eng. Progr. 64 (1968) 31-43.
- 46 W.F. Blatt, A. Dravid, A.S. Michaels and L. Nelson, Membrane Science and Technology, Plenum Press, New York (1970) 47-97.
- 47 D.R. Trettin and M.R. Doshi, Chem. Eng. Commun. 4 (1979) 507-522.
- 48 A.A. Kozinski and E.N. Lightfoot, A.I.Ch.E.J. 18 (1972) 1030-1040.
- 49 R.L. Goldsmith, Ind. Eng. Chem. Fundam. 10, No. 1 (1971) 113-120.
- 50 J.W. Carter and P.G. Newick, The prediction of product flux and its purity in ultrafiltration flow systems. Paper presented to the 6th International Congress of Chemical Engineering, Chemical Equipment Design and Automation, Praha, Czechoslovakia, August 21-25 (1978).
- 51 P. Dejmek, Concentration polarization in ultrafiltration of macromolecules, Ph.D. thesis, Lund University (1975).
- 52 H. Goldsmith and H. Lolachi, O.S.W. Res. Dev. Progr. Rept 727 (1971).
- 53 Welinder, Tekn.l.c. thesis, Dept. Chem. Ind., Technical University of Denmark, Lyngby (1974).
- 54 A.R. Johnson and A. Acrivos, Ind. Eng. Chem. Fundam. 8 (1970) 359, Table correction, *ibid.* 9 (1970) 304.
- 55 D.G. Thomas, W.L. Griffith and R.M. Keller, Desalination 9 (1971) 23.
- 56 H. Lolachi, O.S.W. Res. Dev. Rept 843, U.S. Dept of the Interior (1973).

- 57 E.W. Pitera and S. Middleman, *Ind. Eng. Chem. Proc. Des. Develop.* 12 (1973) 52.
- 58 E.A.G. Hamer, U.S. Patent 3, 425, 562-4, Febr. (1969).
- 59 E.A.G. Hamer and R.L. Kalish, Paper presented at the 2nd O.S.W. Symp. on Reverse Osmosis, Miami, Florida (1969).
- 60 J. Csurny, J.S. Johnson Jr, K.A. Kraus, H.O. Philips, W.G. Sisson and C.G. Westmoreland, Biennial Progress Report for the period 15/3 1968 - 15/3 1970. G.E. Moore and J.S. Johnson Jr. (Eds.) p. 270, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1973).
- 61 M.J. van der Waal, P.M. van der Velden, J. Koning, C.A. Smolders and W.P.M. van Swaay, *Desalination* 22 (1977) 465-483.
- 62 J. Hiddink and R. de Boer, Concentration of milk and whey by reverse osmosis, paper presented at the 2nd International Congress on Engineering and Food, Helsinki, Aug. 27-31 (1979).
- 63 J. Lai, Thesis, Montana State University, Bozeman, Montana, USA (1971).
- 64 R.A. Shaw, R. Delucia and W.M. Gill, *Desalination* 11 (1972) 189-205.
- 65 M. Lopez-Leiva, Ultrafiltration in rotary annular flow, Ph.D. thesis, Lund University (1979).
- 66 T.J. Kennedy, L.E. Monge, B.J. McCoy and R.L. Merson, *Chem. Eng. Prog. Symp. Ser.* 69 (1973) 81.
- 67 T.J. Kennedy, R.L. Merson and B.J. McCoy, *Chem. Eng. Sci.* 29 (1974) 1927.
- 68 W.L. Thayer, L. Pageau and S. Sourirajan, *Can. J. Chem. Eng.* 53 (1975) 422-426.
- 69 H.L. Lee and E.N. Lightfoot, *A.I.Ch.E.J.* 20, No. 2 (1974) 335-339.
- 70 M.R. Doshi, Boundary layer removal in ultrafiltration. Paper presented at the ACS Annual Meeting, Wash. D.C. Sept. 9-14 (1979).
- 71 G. Capobianco, E. Drioli and G. Ragosta, *J. Solid Phase Biochem.* 2 (1977) 315-328.
- 72 M. Cantarella, M.H. Remy, V. Scardi, F. Alfani, G. Iorio, G. Greco Jr, *Biochem. J.* 179 (1979) 15-20.
- 73 F. Alfani, G. Iorio and G. Greco Jr, *Chem. Eng. Sci.* 34 (1979) 1213-1219.
- 74 M. Cantarella, L. Gianfreda, R. Palescandolo, V. Scardi, G. Greco Jr, F. Alfani and G. Iorio, *J. Solid Phase Biochem.* 2 (1977) 163-174.
- 75 J.J.S. Shen and R.F. Probstein, *Ind. Eng. Chem. Fundam.* 16 (1977) 459-465.
- 76 J.R.F. Probstein, J.S. Shen and W.F. Leung, *Desalination* 24 (1978) 1-16.
- 77 N. Epstein, Proceedings of the Int. Conf. on the fouling of Heat Transfer Equipment, Aug. 13-17 (1979), Troy, New York.
- 78 R. Fenton-May, Ph.D. thesis, Univ. of Wisconsin (1971).

- 79 A.J. Wiley, G.A. Dubey and I.K. Bansal, Report to EPA on EPA WQ Contract No, 12040 EEL, Febr. (1972).
- 80 C. Peri and W.L. Dunkley, Part 1 and Part 2, J. Food Sci. 36 (1971) 25-30 and J. Food Sci. 36 (1971) 395-396.
- 81 C. Peri and C. Pompei, Int. Symposium on heat and mass transfer problems in food engineering, Wageningen, Oct. (1972).
- 82 D.C. Sammon and B. Stringer, Process Biochemistry, March (1975) 4-12.
- 83 G. Belfort, Desalination 21 (1977) 285-300.
- 84 L. Leiserson, Proceedings of workshop symposium Membranes in Separation Process, Case Western Reserve University, May (1973) 143-146.
- 85 D. Kuiper, C.A. Bom, J.L. van Hezel and J. Verdouw, Proceedings 4th Int. Symposium Fresh water from the sea, Heidelberg, Aug. 1973, 4 (1973) 207-215.
- 86 J.E. Cruver and I. Nusbaum, Journal WPCF 46 (1974) 301.
- 87 J.W. McCutchan and J.S. Johnson, J.A.W.W.A. 62 (1970) 346.
- 88 J.R. Grover and M.H. Delve, Chem. Eng. 257 (1972) 24-29.
- 89 J.W. Carter, G. Hoyland and A.P.M. Hasting, Chem. Eng. Sci. 29 (1974) 1651-1658.
- 90 J.P. Agrawal, C.R. Antonson and N.W. Rosenblatt, Desalination 11 (1972) 71-90.
- 91 D.L. Feuerstein, Report to EPA on Project 17040 EFC, Contract 14-12-885, Febr. (1971).
- 92 D.L. Feuerstein and Burzstynski, Amer. Inst. Chem. Eng. Sympos. Series 67, 107 (1971) 568.
- 93 J.E. Beckman, E.E. Bevege, J.E. Cruver, S.S. Kremen and I. Nusbaum, OSW Res. Develop. Progress Rept 882, Sept. (1973).
- 94 T.H. Lim, W.L. Dunkley and R.L. Merson, J. Dairy Sci. 54 (1971) 306-311.
- 95 F.A. Glover and B.E. Brooker, J. Dairy Res. 41 (1974) 80-93.
- 96 R.E. Minturn, OSW Res. Develop. Progress Rept 897, Oct. (1973).
- 97 E.E. Bevege, Cruver, J.E., J.G. Kilbridge, S.S. Kremen and A.B. Riedinger, OSW Res. Develop. Progress Rept 883, July (1973).
- 98 J.F. Hayes, J.A. Dunkerley, L.L. Muller and A.T. Griffin, Aust. J. Dairy Technol. 29 (1974) 132-140.
- 99 J.D. Bashow, J.K. Lawson and T.A. Orofino, EPA Report No. EPA-R2-72-103, Dec. (1972).
- 100 A. Watanabe, O. Yoshio, S. Kimura, U. Keiji and S. Kimura, Nippon Shokuhin Kogyo Gakkaishi 26, No. 6 (1979) 260-265.
- 101 B.A. Winfield, Water Research 13 (1979) 561-564.
- 102 J.M. Jackson and D. Landolt, Desalination 12 (1973) 361-378.
- 103 D. Bhattacharyya and R.B. Grieves, NTIS Publ. PB 297 209, May (1979).

- 104 D.N. Lee and R.L. Merson, *J. Dairy Sci.* 58 (1975) 1423.
- 105 C.R. Lee, Ph.D. Thesis, The Ohio State University (1977).
- 106 M.W. Hickey, Thesis, Victoria Inst. Colleges, Melbourne (1976).
- 107 R.E. Ksting, *Synthetic Polymeric Membranes*, McGraw-Hill Book Co., New York, (1971) 12-52, 227-270.
- 108 G. Jonsson and S. Kristensen, *Desalination* 32 (1980) 327-339.
- 109 R.D. Deanin, *Polymer Structure, Properties and Application*, Cahners Books, Boston, Mass. (1972).
- 110 A.S. Michaels, H.J. Bixler and R.M. Hodggers, *J. Colloid Sci.* 20 (1965) 1034.
- 111 T.F. Busby and K. Ingham, *J. Biochem. Biophys. Methods* 2 (1980) 191-206.
- 112 J.A. Palmer, H.B. Hopfenberg and R.M. Felder, *J. Colloid and Interface Sci.* 45 No. 2 (1973) 223.
- 113 H.B. Hopfenberg, J.A. Palmer and R.M. Felder, 166th National Meeting of American Chemical Society, Chicago, Ill., Aug. 26-31 (1973).
- 114 T.I. Pristoupil and M. Kramlova, *Collection Czechoslov. Chem. Commun.* 36 (1971) 3065.
- 115 H. Winters and I.R. Isquith, *Desalination* 30 (1979) 387-399.
- 116 J.A. Howell and O. Velicangil, *Proceedings 2nd Conf. on Biochemical Engineering*, Henniker, New Hampshire, USA, July 13-18 (1980).
- 117 W. Eykamp, *A.I.Ch.E. Symp. Ser.* 74 (1978) 233-235.
- 118 M.P. Freeman, *Colloid and Interface Science*, Vol. V, Academic Press, (1976) 133.
- 119 N. Kaneko and Y. Yamamoto, *J. Chem. Eng. Japan* 9, No. 2 (1976) 158-180.
- 120 D.N. Lee and R.L. Merson, *J. Food Sci.* 41 (1976) 778-786.
- 121 L.L. Muller, J.F. Hayes and A.T. Griffin, *Austr. J. Dairy Technol.* 28 (1973) 70.
- 122 G. Belfort and B. Marx, *Desalination* 28 (1979) 13-30.
- 123 R.G. Gutman, *The Chem. Eng.*, July (1977) 510-513, 521-523.
- 124 J. Hiddink, R. de Boer and P.F.C. Nooy, *J. Dairy Sci.* 63 (1980) 204-214.
- 125 R.F. Madsen, Ph.D. Thesis, Technical University of Denmark, Copenhagen (1976), Elsevier Scient. Publ. Comp. (1977).
- 126 C. Gerndel, Ph.D. Thesis, Techn. Univ. München (1980).
- 127 S. Kimura and S.I. Nakao, *Desalination* 17 (1975) 267.
- 128 J.W. Carter and G. Hoyland, 5th International Symp. on Fresh Water from the sea 4 (1976) 21-29.
- 129 B.R. Smith and R.D. MacBean, *Austr. J. Dairy Technol.*, June (1978) 57.
- 130 J. Melling, *Process Biochemistry*, Sept. (1974) 7-10.
- 131 D.N. Lee and R.L. Merson, *J. Food Sci.* 4 (1976) 403-410.

- 132 H.P. Gregor and C.D. Gregor, *Scientific American* 239 (1978) 88-101.
- 133 H. Nomura, M. Senō, H. Takahashi and T. Yamabe, *Desalination* 29 (1979) 239-246.
- 134 R. Wallace and R. Gable, *Polymer Engineering and Science*, 14, No. 2 (1974) 92-97.
- 135 S.S. Wang, B. Davidson, C. Gillespie, L.R. Harris and D. Lent, *J. Food Sci.* 45 (1980) 700-702.
- 136 K. Spiegler, U.S. Patent Application 950761 (1978).
- 137 K.C. Channabasappa, *Desalination* 18 (1976) 15-42.
- 138 E. Lowe and E.L. Durkee, *J. Food Sci.* 36 (1971) 31-32.
- 139 R.E. Baier, *Proceedings 3rd Int. Congress on Marine Corrosion and Fouling*. Ed: Acker p. 633-639. Evanston Ill. North Western Univ. Press (1973).
- 140 W. Morde and J. Lyklema, *J. Colloid and Interface Sci.* 71, No. 2 (1979) 350-366.
- 141 C. Sandu, Paper presented at the meeting of Wisconsin Section of the Institute of Food Technologists, Nov. 9 (1979), Madison, Wisconsin.
- 142 D. Mahlab, N. Ben Josef and G. Belfort, *Desalination* 24 (1978) 297-303.
- 143 D. Mahlab, N. Ben Josef and G. Belfort, *Chem. Eng. Commun.* 6 (1980) 225-243.

II

SOLUTE ADSORPTION AS A SOURCE OF
FOULING IN ULTRAFILTRATION

By M. López-Leiva and E. Matthiasson

SOLUTE ADSORPTION AS A SOURCE OF FOULING IN ULTRAFILTRATION

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SUMMARY

The process of membrane filtration can be analyzed as a phenomenon of transfer of mass through some resistances in series. These are generally said to be: the membrane, the semisolid gel layer, and the concentration polarization, (concentration boundary layer).

According to the hydrodynamics of the system one or more of these resistances will control the transfer of mass.

Another phenomenon often neglected and which acts as an added resistance to permeate flux is the adsorption of the rejected species onto the membrane surface.

In this paper we will report some experiments done to quantify the influence of macromolecular adsorption on the total resistance to transfer of mass in ultrafiltration.

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1. Introduction

The decrease in transmembrane flux due to fouling is one of the most serious problems in membrane technique. This phenomenon has been studied quite extensively in order to get some understanding about what causes it and how it can be avoided or predicted.

The so-called gel-polarization theory (1,2) has been the most widely accepted model for describing the transmembrane flux in ultrafiltration of macromolecular solutions. According to this model a gel layer is formed on the membrane surface. This happens when the concentration polarization is large enough so the wall concentration reaches the gel concentration of the macromolecular solution. The hydrodynamic resistance of this gel layer controls entirely the transmembrane flux.

In other models the osmotic pressure of the macromolecular solution at the membrane-solution interface accounts for all the resistance to the mass transfer (3,4,5 and 6).

One factor that could be very important and has received little attention is the adsorption of macromolecules on the membrane surface. One would expect that this adsorption affects both the pore size distribution and the surface charge and hydrophilicity of the membrane. This could have great effect on the membrane characteristic and change both its hydraulic permeability and rejection properties.

Michaels et al (7) found that small amounts of polyvinyl methyl ether in the feed solution could increase the salt retention but only with a small accompanying flux decline.

Wong and Quinn (8) observed that when bovine serum albumin (BSA) was present in the solution the diffusive permeability of KCl through a track-etched mica membrane decreased. This decrease was attributed to the adsorption of BSA molecules on the pore walls.

Munch et al (9) found that the hydraulic permeability of track-etched mica membranes decreased after being in contact with BSA solution which was explained by decrease in pore radius due to protein adsorption.

Jonsson and Kristensen (10) observed in ultrafiltration of permeate from membrane filtration of sulphite liquors a decrease in permeate flux which was believed to occur because of a surface adsorption of medium molecular weight organic molecules inside the pores of the membrane.

Howell and Velicangil (11) described the ultrafiltration process as a three stage process with distinctive time constants. In the first stage a quasi-steady-state concentration profile is formed at the membrane surface in less than 5 seconds. In the second stage of one to ten minutes adsorption of the solute on the membrane surface takes place. In the third stage a gel layer is formed on the surface. The flux decline in the adsorption step occurs at a much faster rate than in the gel forming step.

Busby and Ingham (12) observed that the rejection of poly-(ethylen glycol) (PEG) increased when human serum albumin (HSA) was added to the system. This increase in rejection was independent of albumine concentration between 1 and 100 mg/ml and persisted even after albumin was removed. The flux was also lower for the membranes that had been exposed to the albumin solution. Original flux and sieving properties were only restored after treatment of the membrane with trypsin. These facts led to the conclusion that the changes in membrane characterization and performance were due to irreversible adsorption of albumin to the membrane.

Michaels and Lange (13) have studied the adsorption of BSA molecules on the membrane surface. The exposure of Diaflo XM 100 membrane to a BSA solutions of different concentrations without filtration resulted in an irreversible reduction in membrane hydraulic permeability to pure water. Below an exposure-concentration of 1 g/l the permeability decreases rapidly with increasing BSA concentration. Above 1 g/l the permeability declines slowly reaching a limiting value (at approximately 4 g/l) of about half the original pure water permeability of the clean membrane. This limiting value of the permeability reduction suggest saturation of

the membrane surface with protein analogous to Langmuir adsorption resulting in an adsorbed monolayer. It was also found that the rejection coefficient of the membrane for BSA rises as the concentration of BSA that has been in contact with the membrane increases.

It is obvious from the literature reviewed here that strong evidences are for some kind of adsorption that changes considerable both the membrane rejection characteristic and performance. An important factor in protein adsorption is the pH of the solution. The amount of protein adsorbed and the structure of the adsorption layer is sensitive to variation in pH (14). Therefore if the changes in the membrane characteristic when exposed to the protein solution are due to protein adsorption one would expect that these changes are depending on the pH of the solution. If this fact is experimentally verified, a further evidence that protein adsorption causes the changes in membrane performance would be established.

The principal objective of this research is to show the existence of a protein adsorption layer and to determine its importance in the overall resistance to transmembrane flux in ultrafiltration. This work is part of a more comprehensive research on the fouling of UF-membranes. The main aim of this project is to study the fouling mechanism and its dependence on different parameters like surface characteristic, solution properties and flow conditions. For this purpose some different fouling-analyzing techniques like ESCA, ellipsometry and multiple attenuated reflection infrared spectroscopy (MAIR) are going to be used to identify the foulant, as well as to follow the way in which it is formed on the membrane surface.

2. Experimental Methods and Results.

The permeate flux in ultrafiltration can be generally expressed as the quotient between a driving force and an equivalent resistance

$$J = \frac{\Delta P}{R_M + R_A + R_G + R_{BL}} \quad (1)$$

The driving force is the difference of pressure at both sides of the membrane and the equivalent resistance is written as equal to the sum of four resistances in series: the membrane, the adsorbed layer, the gel layer and the concentration boundary layer (Fig. 1). Out of these quantities, the pressure difference, ΔP , and the permeate flux, J , are easily measured in each experiment. The resistance due to the membrane is obtained as usual in a single experiment with pure water. In this case $R_A = R_G = R_{BL} = 0$ and R_M is calculated as

$$R_M = \frac{\Delta P}{PWF} \quad (2)$$

PWF = Pure water flux

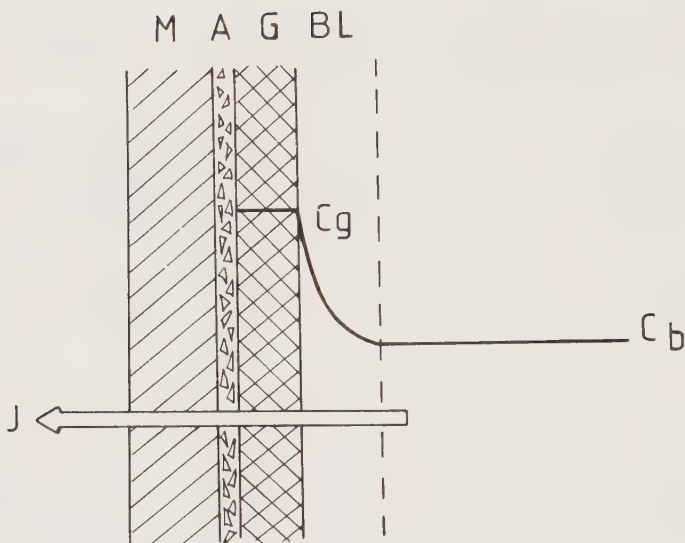


Fig. 1. Transmembrane flux in UF. M = membrane, A = adsorbed monolayer, G = gel layer, BL = concentration boundary layer, J = permeate flux, ΔP = pressure difference, C_g = concentration of gelation, C_b = bulk concentration.

To measure the resistance due to the adsorbed layer, R_A , we had to find a system which was able to diminish the concentration polarization to a negligible value in order to make $R_G = R_{BL} = 0$ in equation 1.

The equipment used was a UF module of rotary type described in detail elsewhere (15, 16) and which has shown good performance in the ultrafiltration of different solutions.

Fig. 2 shows a transverse view of this module. It is composed of a central rotatable hollow tube of 2.6 cm diameter and 60 cm length. This tube supports the semipermeable UF membrane (Kalle E 11, cut off = 20 000).

An external cylinder made of calibrated glass forms with the membrane a 3.5 mm annular gap.

A Rotary membrane
 B Mechanical seals
 D Annular gap
 E Shell
 T Thermocouple

F Feed
 C Concentrate
 P Permeate

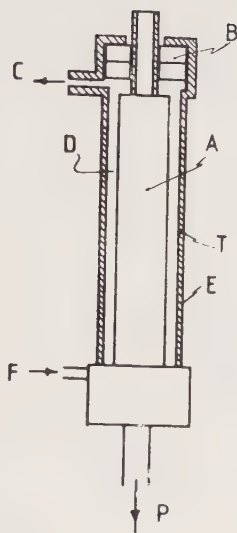


FIG. 2 ROTARY MODULE

In operation, when the membrane is rotating, the solution to be ultrafiltered is pumped at F (Fig 2), it flows in the annulus up to the top of the module where it exits through point C. The low molecular weight components permeate through the membrane and are collected down at P.

The shear stress of this system is controlled by the rotation of the membrane and consequently the axial flow has no significant influence over the transfer of mass. Another advantage with this kind of module is that due to the low axial velocity required the pressure drop along the module is negligible and hence more accurate experiments can be performed.

In a previous work with this module (16) it was seen that at high rotations and moderate concentrations it was possible to ultrafiltrate Bovine Serum Albumin (BSA) in the absence of any detectable concentration polarization. This fact will be used in this work to determine the magnitude of any adsorbed monolayer present in the ultrafiltration of macromolecules.

BSA solutions were ultrafiltered in this module. Two different pH's (4.7 and 6.4) were used to account for the electrical change of the protein. It was expected that the pH of the protein solution would have a significant influence upon R_A due to the different degrees of repulsion between the more or less negatively charged protein molecules and the negatively charged polysulfone membrane surface.

The first experiment was designed to determine the experimental conditions where both the gel layer and the concentration polarization were absent. Starting at the highest velocity and 0.5 MPa pressure, the module was first run with pure water and the pure water flow (PWF) recorded. At a certain time the water was replaced by a 1% BSA solution (pH = 6.4), and the new, steady state, permeate flux measured. The rotation of the membrane (and hence the rate of shear) was diminished and increased several times and the permeate flux recorded at different steady state conditions. The results of this experiment are shown in Fig. 3.

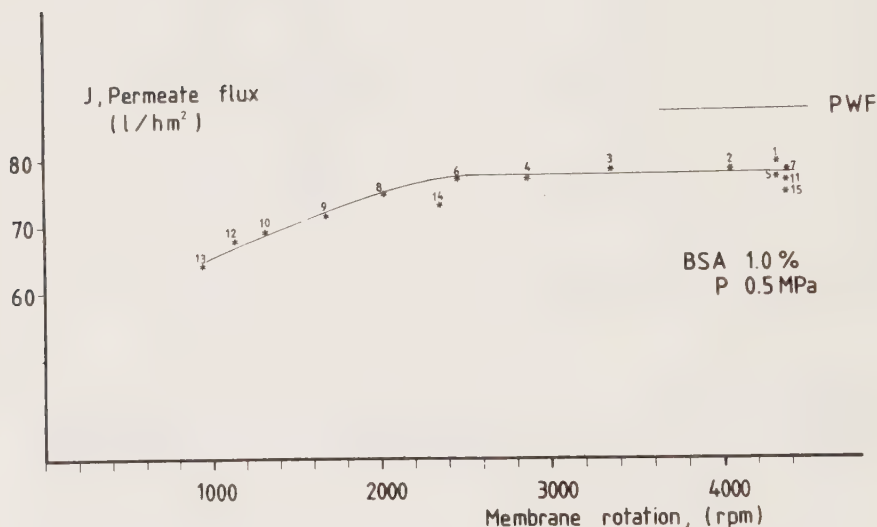


Fig. 3. Permeate flux as function of the velocity of rotation of the membrane. Numbers indicate the order in which the experimental points were taken.

The numbers drawn at each experimental point show the order in which they were taken. We see that there is a plateau which extends down to around 2 500 rpm where the permeate flux does not change. We can move back and forth in this region without any increase or decrease of the resistance to flow (points 1 to 7). If we now move down to around 1 300 rpm (points 8,9,10) we are no longer on the plateau but in a zone where the resistance to flux increases with decreasing rate of shear. But,

when we increase the rate of shear again up to 4 400 rpm we see that the original permeate flux is almost completely restored (point 11). If we continue this process and diminish the velocity of rotation down to around 1 000 rpm (points 12 and 13) and then increase it again to 2 400 rpm (point 14) and finally to 4 400 rpm (point 15) we notice that the original permeate flux is not reached, meaning that an irreversible phenomenon has taken place.

In this experiment we can clearly distinguish three zones:

- a) Non-polarized zone. Between 4 400 rpm and around 2 500 rpm, the ultra-filtration of BSA occurs in the absence of any gel layer and also the shear stress is so high that no influence of the concentration polarization is detected.
- b) Polarized zone. At around 2 500 rpm the contribution of the CP to the total resistance begins to be noticed but the phenomenon is still reversible. proved by the fact that the original flux is restored when the velocity of the membrane is increased.
- c) Gel formation zone. At around 1 000 rpm a gel appears which is only partially swept away by the shear stress when the velocity of the membrane is increased to higher values.

From this experiment it is concluded that in the non-polarized zone the only resistance present, besides that of the membrane, is the resistance due to an adsorbed layer on the membrane, and that this is the resistance that account for the difference in permeate flux between protein solution and pure water.

The experiments that follow were done in this high shear stress zone. To be absolutely sure that we were working in the non-polarized region much milder conditions were chosen; namely, BSA solutions of 0.1% and pressures of only 0.1 MPa.

These experiments were performed at a constant velocity of rotation (3 500 rpm). Starting the module with pure water the PWF was measured. At $t=10$ min, the given solution replaced the water and the evaluation of the permeate flux with time was recorded. After a steady state was reached (aprox 30 min), the BSA solution was replaced by pure water and back again to BSA after a while. This was done to detect if we were dealing with a reversible phenomenon or not. The results of these experiments are plotted in Fig. 4 where we see that the new permeate fluxes obtained at steady state are different for different pH's of the same solution (BSA 0.1%, pH = 4.7 and 6.4). Once the adsorbed layer is consolidated the original PWF is not restored when water replaces the protein solutions, meaning that the BSA layer is irreversible adsorbed to the membrane.

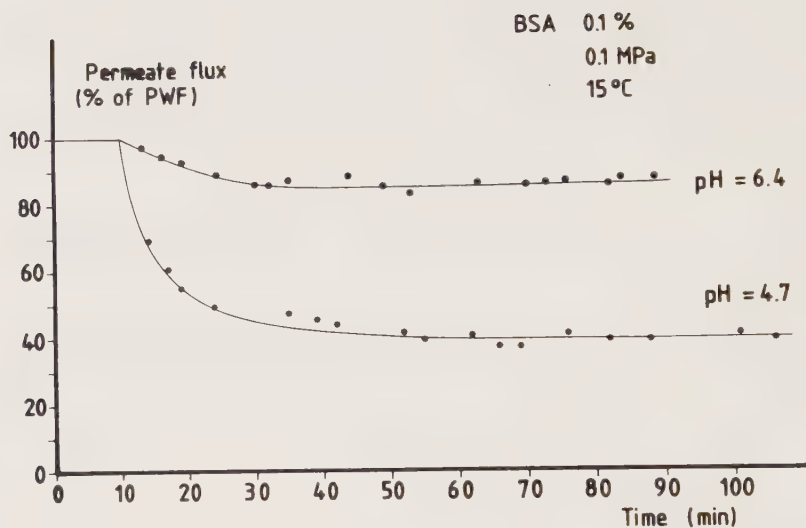


Fig. 4. Ultrafiltration of BSA solutions in the non-polarized region. At $t = 10$ min water is replaced by the BSA solution.

According to eq (1):

$$PWF = \frac{\Delta P}{R_M}$$

$$J_{ss} = \frac{\Delta P}{R_M + R_A}$$

(J_{ss} = steady state value of J for BSA solutions)

and since ΔP is unchanged along the experiment:

$$\frac{R_A}{R_M + R_A} = 1 - \frac{J_{ss}}{PWF}$$

and we can calculate relative values of the resistance due to adsorption (Table 1).

Table 1. Influence of the resistance due to adsorption upon the total resistance to mass transfer.

<u>BSA Solution</u>	$\frac{R_A}{R_M + R_A}$
0.1% pH = 6.4	0.11
1.0% pH = 6.4	0.15
0.1% pH = 4.7	0.62

3. Conclusions

The presence of an adsorbed monolayer in ultrafiltration of a protein solution (BSA) has been detected.

For this we have made use of a rotary ultrafiltration module which is able to produce very high shear stresses allowing us to perform the ultrafiltration in a non-polarized region. There is a strong indication that in this region the only resistances to permeate flux are the membrane itself and the adsorbed monolayer.

The experimental results show that the biggest influence upon the size of this layer is given by the pH of the solution.

At a concentration of 0.1% and 0.1 MPa the resistance due to the adsorbed layer is around 11% of the total resistance when the pH is 6.4, while at pH = 4.7 this value increases to 62%.

Since the surface of the Kalle E 11 membrane is slightly negatively charged we can explain this behaviour by the magnitude of the repulsive forces between membrane surface and protein molecules. The isoelectric point of BSA is 4.7 and hence in the first case (pH = 6.4) the molecules are strongly negatively charged. A repulsive force exists in this case between protein and membrane which makes the BSA molecules less prone to be adsorbed at the membrane surface. At pH = 4.7, in the other case, the net charge density of the protein molecules is zero and a weak repulsion force between membrane and protein makes the adsorption much easier. This is in accordance with results found in the literature (14).

The degree of adsorption is almost not influenced by a ten-fold variation in solution concentration.

At the same pH of 6.4 two BSA solutions were tested. One of 0.1% (Fig. 4) and the other of 1.0% (Fig. 3). We can say that in the second case, the concentration at the wall of the membrane is at least 10 times greater than in the first one, but anyhow the resistance due to the adsorbed protein in both cases is almost the same (11% and 15%). According to some reported works (14) the concentration of adsorbed protein Γ , (g/m^2), becomes independent of the concentration of protein in solution C , (g/m^3) when C becomes greater than a certain minimum value. In our case it means that a BSA concentration of 0.1% is above this minimum value and hence we have worked at the plateau of the Γ vs C curve.

Michaels and Lange (13) have studied the effect of BSA adsorption upon the permeability of a PM 100 ultrafiltration membrane. They studied this phenomenon by exposing the UF membrane, without transmembrane flux, to BSA solutions of different concentrations, and measuring afterwards the pure water permeability. The results they obtained are only partially confirmed by ours. At concentrations higher than about 0.2% they found that the decrease in flux becomes independent of BSA concentration. The reduction in flux obtained (at pH = 7.2) is equal to about 48%. In our case we got about 13% reduction at pH = 6.4. The difference can be attributed to the fact that they used a much more open membrane (cut off = 100 000) and so it is expected that the relative influence of adsorption on the hydraulic permeability must be much bigger.

Bibliography.

1. A. S. Michaels, Chem. Eng. Progr. 64 (1968) 31-43.
2. W. F. Blatt, A. Dravid, A.S. Michaels and L. Nelsen, Membrane Science and Technology, Plenum Press, New York (1970) 47-97.
3. A. A. Kozinski and E.N. Lightfoot, A.I.Ch.E.J. 18 (1972).
4. R.L. Goldsmith, Ind. Eng. Chem. Fundam. 10, No 1 (1971) 113-120.
5. J.W. Carter and P.G. Newick, The prediction of product flux and its purity in ultrafiltration flow systems. Paper presented to the 6th International Congress of Chemical Engineering, Chemical Equipment Design and Automation, Praha, Czechoslovakia, August 21-25 (1978).
6. V.L. Vilker, C.K. Colton and K.A. Smith. Concentration Polarization in Protein Ultrafiltration II. Theoretical and Experimental Study of Albumin Ultrafiltered in an Unstirred Cell, A.I.Ch.E.J. (1981). (in press)
7. A.S. Michaels, H.J. Bixler and R.M. Rodgers, J. Colloid Sci. 20 (1965) 1034.
8. H.J. Wong and J.A. Quinn, Colloid and Interface Sci., Vol. 5, M. Kerker, ed, Academic Press, New York, N.Y. (1976).
9. W.D. Munch, L.P. Zeslar and J.L. Anderson, J. Membrane Sci., 5, 77 (1979).
10. G. Jonsson and S. Kristensen, Desalination 32 (1980) 327-339.
11. J.A. Howell and O. Velicangil, Proceedings 2nd Conf. on Biochemical Engineering, Henniker, New Hampshire, USA, July 13-18 (1980).
12. T.F. Busby and K. Ingham, J. Biochem. Biophys. Methods 2 (1980) 191-206.
13. A.S. Michaels and K.E. Lange "A study of Solvent and Macrosolute Transport Mechanisms in Asymmetric Ultrafiltration Membranes". OWRT Contract No. 14.34.0001-8548. Stanford University, Department of Chemical Engineering. Report dated February 28, 1981.
14. W. Norde. Ph.D thesis, Wageningen University, The Netherlands (1976).
15. B. Hallström and M. López-Leiva. Desalination, 24 (1978) 273-279.
16. M. López-Leiva, Ph.D. Thesis, Lund University, Sweden (1979).

III

THE ROLE OF MACROMOLECULAR ADSORPTION
IN FOULING OF ULTRAFILTRATION
MEMBRANES

By E. Matthiasson

THE ROLE OF MACROMOLECULAR ADSORPTION IN FOULING OF ULTRAFILTRATION MEMBRANES*

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Summary

It is often supposed that fouling in ultrafiltration of macromolecular solutions is caused by gel formation on the membrane. This gel layer arises when the concentration at the surface due to concentration polarization (CP) reaches the solubility limit of the solute. Another aspect of fouling that has received little attention until recently is macromolecular adsorption on the membrane surface. This adsorption affects both the hydraulic permeability and the rejection properties of the membrane.

In this paper the adsorption of bovine serum albumin (BSA) on different membranes is studied. The influence of both solution properties and membrane surface characteristics are investigated in relation to the effects they produce on: (a) adsorption kinetics, (b) amount adsorbed, and (c) hydraulic resistance of the adsorbed layer. The methods used are observation of changes in the flux through the membranes that have been exposed to protein solutions and radiometric measurement of the amount of ^{14}C labelled BSA proteins adsorbed on the membrane surface.

Introduction

Fouling of macromolecular solutes in ultrafiltration is a phenomenon that is very difficult to predict in most cases. The so-called gel-polarization theory [1,2] or modifications of this theory [3,4] are often used to describe the transmembrane flux. According to these models a gel layer is formed on the membrane surface when the wall concentration reaches the solubility limit of the macrosolute due to concentration polarization. At this stage, the permeate flux is limited by the hydraulic resistance of the gel layer. Other properties of the macrosolutes that are taken into account are their highly concentration dependent viscosity, low and concentration dependent self-diffusivity and low osmotic pressure. In spite of relatively good qualitative agreement with experimental data, there are some deviations which are not predicted by these models.

In other models [5–8], the osmotic pressure of the macrosolutes is not

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neglected as was the case above. These have resulted in theories for ultrafiltration that are osmotic pressure limited instead of gel limited.

It is obvious that every model which fully predicts the transmembrane flow in ultrafiltration must take into account all important properties of the macrosolute. However, one important factor that is not included in the models mentioned above is the ability of macromolecules to adsorb at almost any interface, including membranes. This is a thermodynamically spontaneous process which is also generally irreversible [9]. The adsorption on the membrane surface is probably the first step in the fouling process and could have great effect on the membrane characteristics. In a previous work [10,11] adsorption of Bovine Serum Albumin (BSA) is shown to have large influence on the hydraulic permeability of the membrane. Similar effects have been reported by others [12–16]; in most cases it also affects the sieving characteristic of the membrane.

The aim of this work is to study the adsorption of BSA on different kinds of UF membranes. The influence of both solution properties and membrane surface characteristics are investigated in relation to the effects they produce on the adsorption process and the hydraulic resistance of the adsorbed layer. The methods used are observation of changes in flux through the membranes that have been exposed to protein solutions and radiometric measurements of the amount of ^{14}C labelled BSA proteins adsorbed on the membrane surface.

Materials and methods

Water pretreatment

The water used in the experiments was, unless otherwise indicated, deionized and distilled followed by filtration through a membrane with a cut off of 1 000 daltons. To prevent bacterial growth, sodium azide (0.02 wt%) was added to the water.

BSA solutions

The BSA proteins were purchased from Sigma Chemical Company, product no. A 7511. This is highly purified "Essentially Fatty Acid Free" bovine albumin. The solutions of BSA used in the experiments were prepared in 0.15 M NaCl water solution. The pH of the solution was adjusted with either hydrochloric acid or sodium hydroxide solution. The concentration of the BSA solution was measured in a UV spectrophotometer at 278 nm.

Membranes

Six different commercially manufactured UF membranes were used in the experiments (Table 1). All the membranes should have total rejection for bovine serum albumin protein that has a molecular weight of 68 000 daltons.

TABLE 1

Membrane*	Material	Molecular cut off (daltons)	Initial fluxes** (0.15 M NaCl) (l/m ² -hr)
I	Cellulose acetate (CA)	6 000	50 ± 8
II	Cellulose acetate (CA)	20 000	82 ± 16
III	Polysulfone (PS)	6 000	24 ± 10
IV	Polysulfone (PS)	20 000	50 ± 5
V	Polysulfone (PS)	20 000	160 ± 35
VI	Polyamide (PA)	10 000	61 ± 19

*Membrane I to IV are manufactured by the Danish Sugar Corporation, Denmark.

Membrane V is manufactured by Kalle Niederlassung der Hoechst AG, and VI by Berghof GmbH, F.R.G.

**Data measured at pH 7, 25°C and 0.25 MPa for membranes I to III and 0.10 MPa for IV to VI.

Adsorption experiments

Hydraulic resistance of the adsorption layer

These experiments were performed in a standard circular ultrafiltration batch cell manufactured by Amicon Corporation, with an effective membrane area of 35.3 cm² and total volume of 400 ml. The cell was thermostated in a water bath at 25°C and pressurized with nitrogen through a water reservoir. The cell pressure was 0.25 MPa for membranes I to III and 0.10 MPa for the others. A stop watch and a 10 ml graduated pipette were used to measure the permeate flow. By using distilled and ultrafiltered water with a 0.22 µm filter before the membrane cell as a last precaution, stable water fluxes were obtained usually within 1 to 2 hours. These fluxes remained constant for hours. The experimental set-up is shown in Fig. 1. The experiments were run according to the following procedure: (1) The hydraulic permeability of the membrane to pure 0.15 M NaCl aqueous solution was measured at constant pressure and temperature (0.10 or 0.25 MPa and 25°C). (2) The pressure was relieved

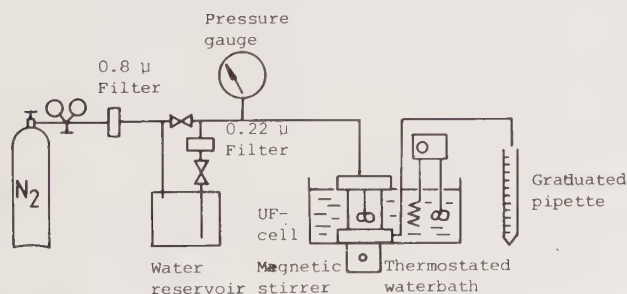


Fig. 1. The experimental set-up for the measurements of the hydraulic permeability.

and the saline water solution was replaced by a BSA solution. The BSA solution remained in contact with the membrane without any filtration for a certain time. (3) The protein solution was washed out with pure saline water solution and the hydraulic permeability of the membrane was measured again.

Adsorbed amount of BSA

In these experiments ^{14}C labelled BSA protein was used to measure the amount adsorbed to the membrane surface. The protein was labelled through reductive alkylation with ^{14}C -formaldehyde, according to the procedure described by Dottavio-Martin and Ravel [17]. This is a rapid method performed under mild conditions (pH 7) which produces a minimal change in the physicochemical structure of most proteins [18–20]. To 1.875 ml of 1.6% solution of BSA protein in 0.04 M potassium phosphate buffer, pH 7.0, made of double distilled water, 0.375 ml (375 μCi) of ^{14}C -formaldehyde was added. This was followed by addition of 0.750 ml of freshly prepared solution of NaBH_3CN (6 mg/ml) in the same buffer as above. The mixture was incubated at 25°C for 4 hours. Afterwards the low molecular weight components were removed by dialysis over a two to three day period at 4°C . This gave a BSA solution of approximately 3 ml and 1% concentration with a radioactivity of $14\text{--}18 \times 10^6$ cpm/mg.

The adsorption experiments with the ^{14}C labelled BSA proteins were carried out in a specially constructed cell with a 9 cm^2 membrane area and a total volume of 0.27 ml (Fig. 2). The experiments were run according to the following procedure: (1) The cell was assembled with the membrane and filled with saline water solution (0.15 M NaCl). (2) The ^{14}C -BSA solution was injected at a constant velocity with a motor driven syringe (Fig. 2) through one end of the cell until the same concentration as injected came out of the other end. (3) The BSA solution remained in contact with the membrane for a certain period of time and was then washed out by injecting pure saline water solution. (4) The cell was dismantled and the membrane removed.

The amount of protein adsorbed on the membrane was analyzed in a scintillation detector after addition of 15 ml of Aquasol scintillation fluid. The cellulose acetate membranes were dissolved in 2 ml of a ethylenglycol-monomethylether solution before adding the scintillation fluid in order to avoid any quenching effect from the membrane. The polysulfone and polyamide membranes were not dissolved in this solvent. This gave 5% lower counting efficiency which was accounted for in the calculation.

Relative flux and adsorption

The permeate flux of the membrane that has been exposed to the BSA solution has been compared to the permeate flux for the unexposed membrane, i.e.

$$RF = J_A / J_0$$

where RF = relative permeate flux; J_A = permeate flux for the membrane

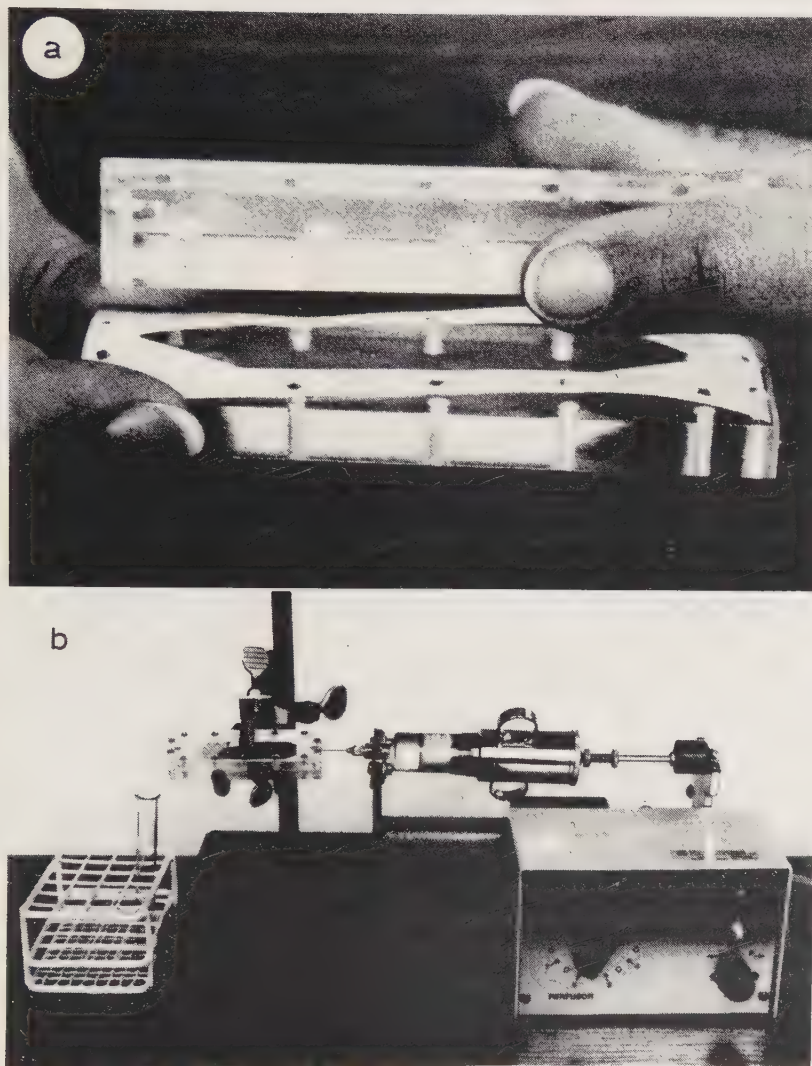


Fig. 2 (a) Cell used for ^{14}C -BSA experiments. The total volume of the cell is formed by the 0.3 mm teflon gasket between the two pieces of plexiglas. The membrane is placed on the solid plexiglas under the gasket with the active side upwards. As there is no outlet for the permeate no flux through the membrane is possible. (b) Experimental set-up for the ^{14}C -tests. The motor driven syringe is connected to the cell.

after adsorption; J_0 = permeate flux for the membrane before adsorption. Both J_A and J_0 are measured at the same pressure and temperature. The relative reduction in the permeate flux due to adsorption can then be expressed as $1-RF$.

In ultrafiltration, the permeate flux, J , can be expressed according to the equation

$$J = \Delta P / R_{\text{Tot}}$$

where ΔP is the driving pressure and R_{Tot} is the sum of the four resistances in series; the membrane R_M , the adsorbed layer R_A , the gel layer R_G and the concentration boundary layer R_{BL} . In this case R_G and R_{BL} are zero and $J = J_A$. The pressure difference, ΔP , is equal to pressure drop over the membrane ΔP_M , and the adsorbed layer ΔP_A . Thus

$$\Delta P = \Delta P_M + \Delta P_A = R_M J_A + R_A J_A$$

Since $R_M = \Delta P / J_0$ the above equation can be written in the form:

$$\Delta P (1 - J_A / J_0) = R_A J_A$$

If the resistance of the adsorbed layer is proportional to the amount adsorbed, M_A , the above equation can be written in the form:

$$\Delta P (J_0 - J_A) / J_0 = c M_A J_A$$

where $c = \text{constant}$, or

$$\Delta P (J_0 / J_A - 1) / J_0 = c M_A$$

Since $(J_0 / J_A - 1) = (1 / RF - 1) = [(R_M + R_A) / R_M - 1] = R_A / R_M$, which is the relative resistance of the adsorbed layer, the above equation can be written in the form:

$$(1 / RF - 1) = R_A / R_M = \frac{c J_0}{\Delta P} M_A$$

Thus, at constant pressure, $(1 / RF - 1)$, which is the relative resistance of the adsorbed layer, is in linear relationship with the amount adsorbed, M_A .

Results and discussion

Support side adsorption

In the measurements of the amount of BSA that adsorbs on the membrane, it was observed that some radioactivity exists on the support side of the membranes. Calculations on the dilution obtained under the dialyses of the ^{14}C -labelled protein solution indicate that this cannot be caused by radioactive carbon free from albumin. Therefore this must be caused by BSA proteins. This adsorption shows a very large variation (see Table 2) but the following tendency has been noticed. There is an increase with increasing BSA concentration and the time of exposure of the membrane to the BSA solution. The amount adsorbed is on the same level for all the membranes except membrane V which presents considerably higher adsorption. The effect of pH on the amount adsorbed is very small, with a slight decrease at pH 3 for the CA membranes and an increase for the PS membranes. As the membranes should have 100% rejection of BSA proteins, this indicates that no membrane is entirely free from defects. Even though

TABLE 2

Membrane	Typical support side adsorption (pH = 7.0)	
	mg BSA/m ²	Percentage of total ads.
I	0.05–0.2	10–35
II	0.05–0.2	20–30
III	0.01–0.2	1–10
IV	0.01–0.2	0.1–3
V	1–7	10–20
VI	0.01–0.3	0.0–0.3

the defects are so small that BSA concentration in the permeate is undetectable with our measuring method, this extremely low concentration causes an adsorption that is observable. This is probably due to the large surface area on the porous support side of the membrane. To avoid these errors, a membrane with the support side upwards was always placed under the other membrane. The amount adsorbed on it was assumed to be the same as was adsorbed on the support side of the membrane above, due to the fact they were exposed to the same low BSA concentration under the same conditions. This support side adsorption was deduced from the total adsorption.

Concentration dependence

As can be seen in Table 1, the initial fluxes for all of the membranes show a very large variation. These variations were observed even if the pieces of membrane used came from the same sheet of membrane. The reason for this uneven distribution of hydraulic permeability is unclear, but it did not affect the reduction in flux due to adsorption when calculated on a relative basis.

The results of the experiments in the study of the influences of BSA concentration on the membrane permeability are shown in Figs. 3 and 4.

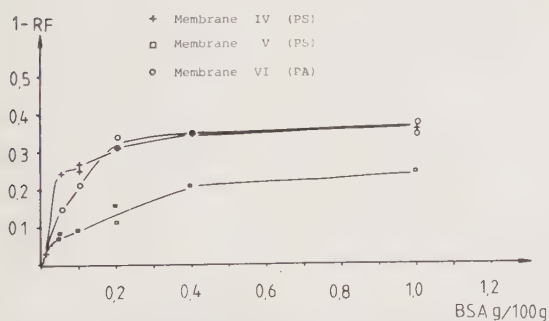


Fig. 3. Influence of the BSA concentration on the relative flux reduction in filtration of a pure saline water solution (0.15 M NaCl, pH 7.0 and 25°C). The BSA solutions have been exposed to the membranes without filtration for 3 hr.

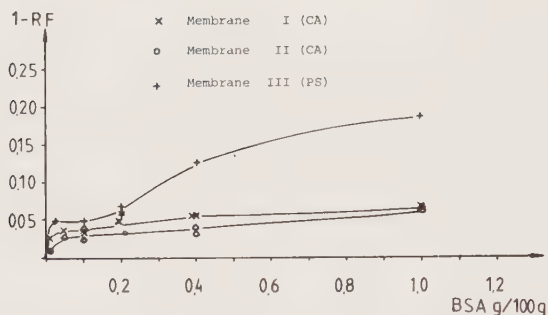


Fig. 4. Influence of the BSA concentration on the relative flux reduction in filtration of a pure saline water solution (0.15 M NaCl, pH 7.0 and 25°C). The BSA solutions have been exposed to the membranes without filtration for 3 hr.

In these figures the relative flux reduction ($1-RF$) is plotted against the concentration of BSA. The results show that the fluxes through the polyamide and the polysulfone membranes are affected much more by the adsorption than the flux through the cellulose acetate membranes. It also appears that the degree of flux reduction varies more between the three polysulfone membranes than between the cellulose acetate membranes, which present almost the same reduction. It is interesting to notice that all these adsorption curves show two distinct steps; the first semi-plateau, in the region between 0.05 and 0.2% concentration of the BSA solution, is more distinct for the polysulfone membranes than for the others.

The corresponding results from the measurements of the amount adsorbed as a function of BSA concentration are presented in Figs. 5 and 6. These adsorption isotherms show a good correlation with the hydraulic resistance measurements. The inflection point in the adsorption curves is even more clearly noticed here, which further indicates that there are at least two distinct steps in the adsorption process. The amount adsorbed at this first semi-plateau is in the range of reported values of monomolecular layers of BSA

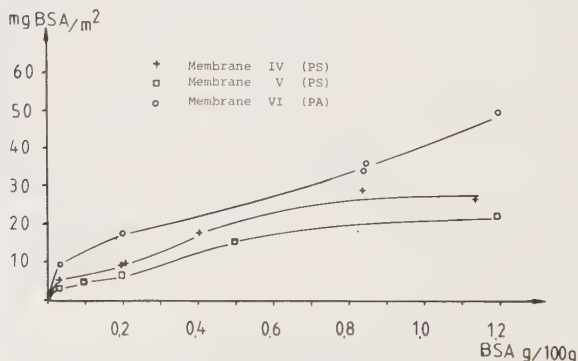


Fig. 5. Adsorption isotherms for BSA on UF-membrane surfaces (pH 7.0, 25°C, 3 hr).

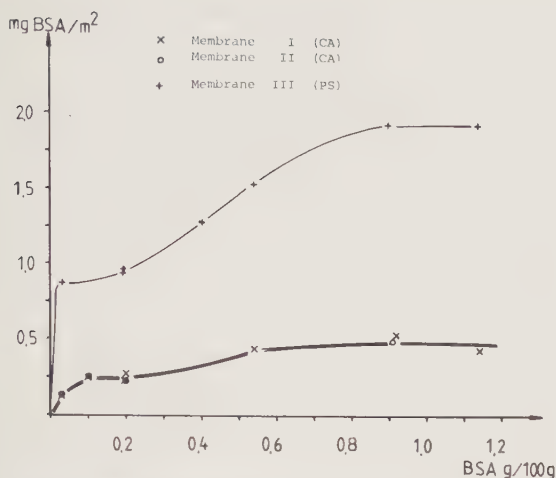


Fig. 6. Adsorption isotherms for BSA on UF-membranes surfaces (pH 7.0, 25°C, 3 hr).

protein adsorbed on solid surfaces. The difference between the two polysulfone membranes IV and V in relation to III is remarkable; this suggests that membranes made out of the same kind of polymer can have quite different surface characteristics. The adsorption isotherms for the two cellulose acetate membranes are identical and parallel the hydraulic measurements where the semi-plateau values are at a much lower level than for the other membranes.

As can be seen in Figs. 3 and 4, the reduction in flux is in the range of maximum 5% for the cellulose acetate membranes to a maximum of 35% for the polysulfone and polyamide membranes. From this, it is clear that adsorption plays an important role in the flux reduction of ultrafiltration. The hydraulic resistance of the adsorbent can be on the same level as that of the gel and concentration polarization layers. The tests show that a plateau value is usually attained at BSA concentrations below 1% in the solution. Under actual ultrafiltration conditions the concentration at the membrane surface is usually much higher. What happens at the membrane surface under these conditions remains unanswered. As a rule [9], experimental adsorption isotherms show that plateau levels are reached at low bulk concentrations, like those applied in these tests.

As mentioned earlier, the cell used in these experiments was filled with the saline water solution before the injection of the radio-labelled BSA solution. In a few experiments carried out with membrane I (CA), the cell was filled with air instead of saline water solution when a BSA solution (0.04 g/100 g) was injected. The membrane that had previously been soaked in the saline water solution was still humid at the time the cell was filled with the BSA solution. The results from these experiments show that the amount adsorbed when the cell was filled with air was two to three times larger than when it was filled with the saline water solution, which is on the same level as the maximum of the adsorption isotherm for membrane I in Fig. 6. An explanation for

this increase in adsorption may be found in the fact that a three phase contact between solid membrane, air and BSA solution is established at the membrane—moving water boundary. As proteins are known to unfold at liquid—air interfaces, a contact is therefore established between denaturated proteins and a surface that probably is more hydrophobic than usual due to the contact with air. Under these circumstances an increase in adsorption is expected as these changes of the protein and the surface are known to promote adsorption.

pH dependence

The results of the experiments studying the influence of the pH of the BSA solution on permeate flux and the amount adsorbed are shown in Figs. 7 and 8. In these tests the adsorption time was one hour, which is enough

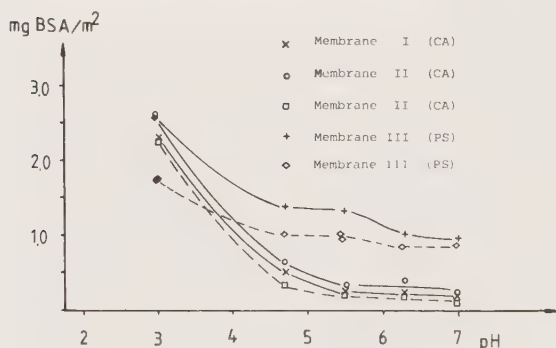


Fig. 7. Influence of the pH of the BSA solution (— 0.2 g/100 g, --- 0.04 g/100 g) on the amount adsorbed on the UF-membrane surfaces (1 hr, 25°C).

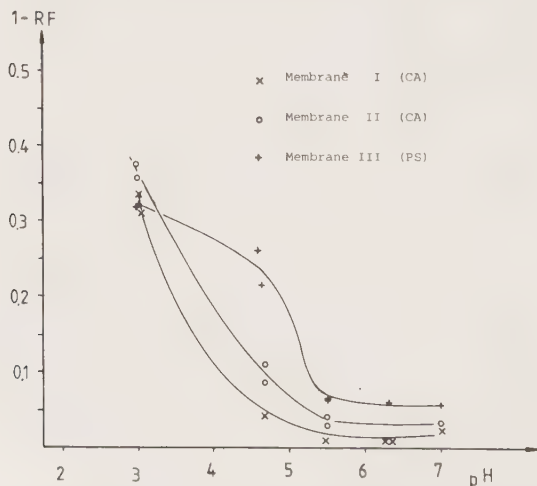


Fig. 8. Influence of the pH of the BSA solutions (0.2 g/100 g) on the relative flux reduction in filtration of a pure saline water solution (0.15 M NaCl, and 25°C). The BSA solutions have been exposed to the membranes without filtration for 1 hr.

to reach the maximum plateau value (see adsorption kinetics). The initial fluxes below pH 7.0 were in the same range of the fluxes shown in Table 1 for all membranes except membrane II at pH 3.0, which consequently presented about 25% lower fluxes ($61 \pm 5 \text{ l/m}^2\text{-hr}$). The agreement between these two experiments is quite good. As can be seen from the figures, the amount and the hydraulic resistance of the adsorbed layer increases as the pH of the solution is decreased. Between pH 4.7 and 3.0, both the hydraulic resistance and the amount adsorbed increase quite suddenly. Both the cellulose acetate and the polysulfone membranes are negatively charged. Above the isoelectric point (pH = 4.7) the BSA protein is also negatively charged. Its negative charge decreases successively as the pH comes closer to the isoelectric point. This should also successively decrease the repulsive forces that are acting between the negatively charged membrane and the proteins, which can explain the increase in adsorption when the pH of the solution comes closer to the isoelectric point. Beyond the isoelectric point, the proteins become positively instead of negatively charged, so the forces between the BSA molecules and the membrane surfaces that were repulsive when the pH was over 3.7 now become attractive. This should act in favor of further increase in adsorption below the I.E.P., which is in agreement with the experimental results. Another fact that could contribute to the increase in adsorption at lower pH is the unfolding of the BSA protein that takes place below pH 5. Changes in surface characteristics of the membrane at different pH could also have some influence on the adsorption. These are somewhat more difficult to predict, but it is known that the negative charge decreases with decreasing pH.

Adsorption kinetics

The results from the study of the adsorption kinetics are shown in Figs. 9 and 10. The agreement between the amount adsorbed and the increase in

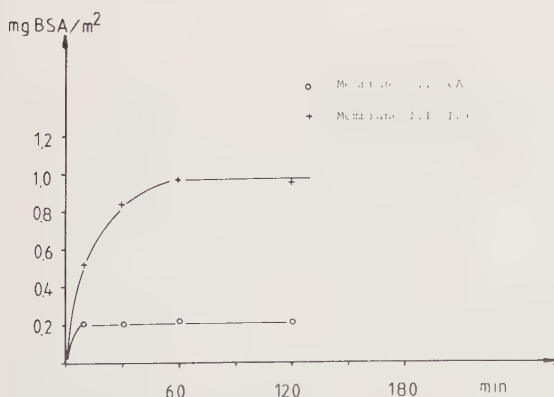


Fig. 9. The adsorption of BSA (0.2 g/100 g) on UF-membrane surfaces as a function of time.

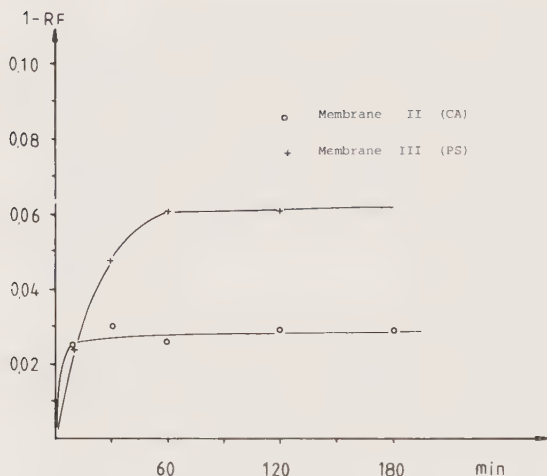


Fig. 10. Influence of BSA (0.2 g/100 g) as a function of time on the relative flux reduction in filtration of a pure saline water solution (0.15 M NaCl, pH 7.0 and 25°C). The BSA solutions have been exposed to the membrane without filtration.

hydraulic resistance as a function of time is quite good. It can be seen from these figures that after 10 minutes the adsorption of the BSA on the cellulose acetate membrane has already attained the plateau value, while this takes around 1 hour for the polysulfone membrane. This indicates that there is some difference in the adsorption mechanism of the BSA protein on these two different kinds of polymers.

Hydraulic resistance and membrane adsorption

It is quite clear from all the experiments (Fig. 3–10) that there is a strong relationship between the amount of BSA adsorbed and the reduction in hydraulic permeability.

In Figs. 11 and 12, $1/RF-1$ which is the relative resistance of the adsorbed layer is plotted as a function of the amount of BSA adsorbed according to the experimental results in Figs. 3–6.

As can be seen from these figures, a clear linear relationship exists. In the case of the membranes III to VI, there is a linear relationship up to a certain amount adsorbed followed by a very sharp breakpoint. Above this breakpoint there is another linear relationship but the slope of this line is much lower. The breakpoint for all of the membranes is around the transition stage from the first to the second step in the adsorption process which was mentioned earlier. This gives an indication that there is a difference in the structure of the protein layer adsorbed in the first step and that adsorbed in the second step. This kind of breakpoint is not observed for the cellulose membranes in Fig. 11. As the reduction of the permeate flow for these membranes is very low, the standard deviation of the measurements is not as good as in the other experiments. It is therefore difficult to determine whether or not there is a breakpoint.

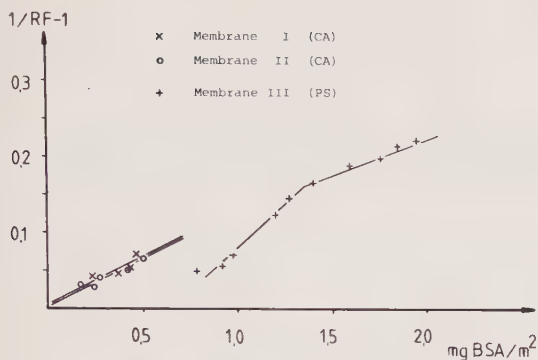


Fig. 11. Relative resistance of the adsorbed BSA on the membrane surfaces versus the amount adsorbed.

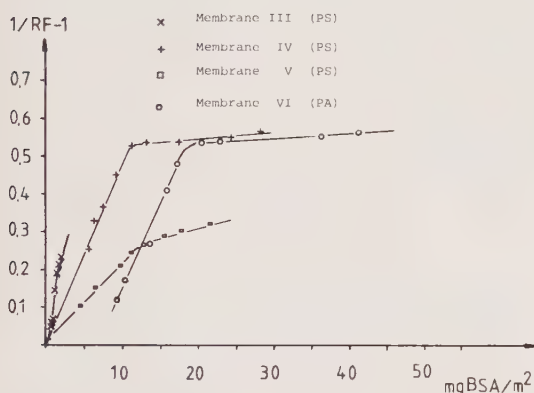


Fig. 12. Relative resistance of the adsorbed BSA on the membrane surfaces versus the amount adsorbed.

Conclusions

The results indicate that there are at least two distinct steps in the adsorption process of BSA protein on the UF membrane surfaces. The hydraulic resistance increases linearly with the amount adsorbed for both the first and second step of the adsorption process, but more rapidly for the first.

The cellulose acetate membranes adsorb less protein than the polyamide and the polysulfone membranes, and as a consequence of this, the permeate flux is substantially less affected.

When air is in contact with both the membrane and the BSA solution the amount adsorbed increases considerably.

The adsorption is strongly pH dependent and increases with decreasing pH of the solution.

References

- 1 A.S. Michaels, New separation technique for the CPI, *Chem. Eng. Progr.*, 64 (1968) 31–43.
- 2 W.F. Blatt, A. Dravid, A.S. Michaels and L. Nelsen, Solute Polarization and Cake Formation in Membrane Ultrafiltration: Causes Consequences and Control Techniques, *Membrane Science and Technology*, Plenum Press, New York, 1970, pp. 47–97.
- 3 J.R.F. Probst, J.S. Shen and W.F. Leung, Ultrafiltration of macromolecular solutions at high polarization in laminar channel flow, *Desalination*, 24 (1978) 1–16.
- 4 D.R. Trettin and M.R. Doshi, Limiting flux in ultrafiltration of macromolecular solutions, *Chem. Eng. Commun.*, 4 (1979) 507–522.
- 5 A.A. Kozinski and E.N. Lightfoot, Protein ultrafiltration: A general example of boundary layer filtration, *AIChE J.*, 18 (Nov.) (1972) 1030–1040.
- 6 R.L. Goldsmith, Macromolecular ultrafiltration with microporous membranes, *Ind. Chem. Fundam.*, 10, (1) (1971) 113–120.
- 7 J.W. Carter and P.G. Newick, The prediction of product flux and its purity in ultrafiltration flow systems. Paper presented to the 6th International Congress of Chemical Engineering, Chemical Equipment Design and Automation, Prague, Czechoslovakia, August 21–25, 1978, Czechoslovakian Chemical Society, Committee for Industrial Chemistry.
- 8 V.L. Vilker, C.K. Colton and K.A. Smith, Concentration polarization in protein ultrafiltration, II, theoretical and experimental study of albumin ultrafiltered in an unstirred cell, *AIChE J.*, 27 (4) (1981) 637–645.
- 9 W. Norde, Proteins at interfaces, Ph.D. Thesis, Wageningen University, The Netherlands, 1976.
- 10 M. López-Leiva, Ultrafiltration in rotary annular flow, Ph.D. Thesis, Lund University, Sweden, 1979.
- 11 M. López-Leiva and E. Mathiasson, Solute adsorption as a source of fouling in ultrafiltration, in: B. Hallström, D.B. Lund and Ch. Trägård (Eds.), *Proc. from the International Workshop on the Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing*, Tylösand, Sweden, 1981, Lund University Press, pp. 299–308.
- 12 W.D. Munch, L.P. Zestar and J.L. Anderson, Rejection of polyelectrolytes from microporous membranes, *J. Membrane Sci.*, 5 (1979) 77–102.
- 13 G. Jonsson and S. Kristensen, Membrane filtration of NSSC-waste liquor, *Desalination*, 32 (1980) 327–339.
- 14 J.A. Howell and O. Velicangil, in: K. Venkatsubramanian (Ed.), *Proc. of 2nd Conf. on Biochemical Engineering*, Henniker, New Hampshire, USA, July 13–18, 1980.
- 15 T.F. Busby and K.C. Ingham, Separation of macromolecules by ultrafiltration: Removal of poly (ethylene glycol) from human albumin, *J. Biochem. Biophys. Methods*, 2 (1980) 191–206.
- 16 A.S. Michaels and K.E. Lange, A study of solvent and macrosolute transport mechanisms in asymmetric ultrafiltration membranes, OWRT Contract No. 14.34.0001-8548, Stanford University, Department of Chemical Engineering, Report dated February 28, 1981.
- 17 D. Dottavio-Martin and J.M. Ravel, Radiolabeling of proteins by reductive alkylation with (^{14}C) formaldehyde and sodium cyanoborohydride, *Anal. Biochem.*, 87 (1978) 562–565.
- 18 R.H. Rice and G.E. Means, Radioactive labelling of proteins in vitro, *J. Biol. Chem.*, (1971) 831–832.
- 19 G. Moore and R.C. Crichton, Reductive methylation: a method for preparing functionally active radioactive ribosomes, *FEBS Lett.*, 37 (1) (1973) 74–78.
- 20 G.E. Means and R.E. Fenney, Reductive alkylation of amino groups in proteins, *Biochemistry*, 7 (6) (1968) 2192–2201.

IV

ADSORPTION PHENOMENA IN FOULING
UF-MEMBRANES

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ADSORPTION PHENOMENA IN FOULING UF-MEMBRANES

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ABSTRACT

Fouling is, due to its negative influence on the flux, a serious problem in ultrafiltration operations. The whole fouling phenomena is extremely complicated and in many ways not fully understood. There is a reason to believe that one of the most important factors involved is the adsorption of macromolecules on the membrane surface. This adsorption that is a thermodynamically spontaneous process is probably the first step in the fouling process.

In this paper studies of this phenomena are presented. The reduction in the flux of pure buffer solutions through membranes that have been exposed to high solute concentrations of bovine serum albumin (BSA) is investigated. The importance of this decrease in permeability when predicting the transmembrane flux is studied and an empirical equation giving the reduction in permeability as a function of solute concentration of the protein is presented. Finally the relationship between the amount of protein adsorbed or coagulated on the membrane surface and the resistance it produces is analysed.

INTRODUCTION

Fouling in ultrafiltration is a well known phenomenon which often causes serious limitations for this unit operation.

In spite of the fact that this phenomenon has been studied quite intensively during the last ten to fifteen years there are still many factors that influence the fouling process and that are not fully understood.

Most theories that have been developed in order to explain and predict the fouling process are based on the solute properties and the flow conditions above the membrane surface.

Among these theories the so-called gel-polarization theory (1) or modifications of it are most often used (2,3). According to these theories a gel layer is formed on the membrane surface when the wall concentration reaches the solubility limit of the macrosolute. At this stage the transmembrane flux is said to be entirely depending on the resistance of this gel layer and the back-diffusion of the macrosolute in the concentration boundary layer.

In other theories (4-6) it is claimed that the osmotic pressure of the macrosolute can not be neglected. These analyses have resulted in models where the osmotic pressure of the polarized layer limits the transmembrane flux.

Either the theories are based on the gel-polarization model or the pure osmotic pressure model the qualitative agreement with experimental data are usually quite good. Nevertheless there are many experimental facts that are not predicted by these theories.

As mentioned before the theories outlined above take into account the flow conditions and the properties of the macromolecular solution. One factor that is not included is the interaction between the macrosolute and the membrane surface. In our previous work (7,8) and others (9-11) it has been shown that macromolecular adsorption on the membrane surface can strongly affect both the transmembrane flux and the separation characteristics. It is well known that macromolecules have a strong tendency to adsorb at almost any interface. Adsorption at solid-liquid as well as other interfaces has

been studied intensively for a long time. This is a very complicated phenomenon and there are still many factors that are unknown or have no definite answers. In general one can say that adsorption at solid-liquid interfaces is very much depending on solution properties (pH, ionic strength, concentration of solute) and surface characteristics (hydrophilicity, hydrophobicity, surface charge).

Experimental studies have shown that adsorption of proteins increases with increasing concentration in solution to reach well-established plateau values at concentration usually below 0.1 wt%. The amount adsorbed at these plateau values usually corresponds to a monomolecular layer of the proteins (12). Measurements at much higher concentrations are quite rare and those we find regarding a membrane surface in an ultrafiltration process have never been considered. Measurements at 1% concentration have shown that for hydrophobic surfaces much more protein than the observed plateau value around 0.1% can adsorb or coagulate (13).

The objective of this work is to measure the adsorption or coagulation of proteins on UF-membrane surfaces at high solute concentrations and investigate how the transmembrane flux is affected.

MATERIALS AND METHODS

Experiments were performed in order to measure the reduction in the permeate flux of membranes that had been previously exposed to high concentration of Bovine Serum Albumin (BSA) protein solutions as well as to measure the amount that has adsorbed or coagulated onto the membrane surface.

The BSA used in the experiments was highly purified "Essentially Fatty Acid Free" protein purchased from Sigma Chemical Company, product no A 7511. The protein solutions were all made in 0.15 M NaCl solutions at pH 7.

The water used for the experiments was prefiltered through an ultrafiltration membrane (molecular cut off of 1000 dalton) after distillation and deionization. As a final purification step all solutions passed through a 0.22 μm filter before entering the batch cell. In order to prevent bacterial growth 0.02 wt% sodium azide was added.

Three commercial membranes made out of different polymers (see Table I) were used in the experiments. The polysulfone and polyamide membranes are both hydrophobic while the cellulose acetate one is hydrophilic.

Table I .

Membrane*	Material	Molecular cut off (daltons)	Initial fluxes ($\text{l/m}^2 \text{ h}$)
I	polyamide (PA)	10 000	56.7 ± 4.4 (0.10MPa)
II	polysulfone (PS)	20 000	39.7 ± 5.5 (0.10MPa)
III	cellulose acetate (CA)	20 000	74.0 ± 10.5 (0.25MPa)

* Membrane I is manufactured by Berghof GmbH, F.R.G. and membrane II and III by the Danish Sugar Corporation, Denmark.

The measurements of the reduction in permeate flux were done in a standard circular ultrafiltration batch cell with an effective membrane area of 4.23 cm^2 and total volume of 20 ml. In these experiments, which have been described in detail elsewhere (8), the fluxes for pure 0.15 M NaCl solution of pH 7 and 25°C were measured at either 0.10 or 0.25 MPa (see Table 1), before and after the membranes had been exposed to the protein solutions. The membranes were in contact with the BSA solution for one hour at 25°C. During the adsorption time the cell was not pressurized so no filtration could take place.

In the measurements of the amount of BSA that adsorbed on the membrane surface ^{14}C -labelled protein was used. The protein was labelled through reductive alkylation with ^{14}C -formaldehyde according to Dottavio-Martin and Ravel (14). To 3 ml of an approximately 55% BSA solution in 0.04 M potassium phosphate buffer pH 7.0, 25 μl , (400 μCi) of ^{14}C -formaldehyde and 75 μl of NaBH_3CN (60 mg/ml) were added. This solution was incubated for 4 hours at 25°C and 12 hours at $3-5^\circ\text{C}$. During the time of incubation the solution was stirred mechanically. Afterwards the solution was dialysed for two to three days in order to remove all formaldehyde that had not bound to the protein. The membranes were exposed to the ^{14}C -BSA solution for one hour and the amount BSA that had adsorbed was analysed afterwards in an scintillation detector.

All permeate fluxes after the adsorption have been related to the permeate fluxes before adsorption, i.e.

$$\text{RF} = J_A/J_O \quad (1)$$

where RF = relative permeate flux

J_A = permeate flux after adsorption

J_O = permeate flux before adsorption

Normally in ultrafiltration processes the transmembrane fluxes in the pre-gel region can be expressed by the following equation.

$$J_V = L_p (\Delta P - \sigma \pi) \quad (2)$$

where J_V = actual permeate flux in an ultrafiltration process

π = osmotic pressure of the solution

σ = rejection coefficient

ΔP = applied pressure

L_p = the hydraulic permeability of the membrane

The hydraulic permeability L_p can be written as

$$L_p = \frac{1}{R} = \frac{1}{R_M + R_A} \quad (3)$$

where R is the sum of the resistance of the membrane R_M and the adsorption layer R_A .

R_M can be assumed to be constant during the filtration while R_A which is the resistance caused by the adsorption of the solute on the membrane is depending on the solute properties i.e. concentration, pH and the ionic strength. Thus $R_A = f(c, \text{pH}, \text{ionic strength})$. Usually both pH and the ionic strength are constant during the ultrafiltration process. In this case R_A can be written as a function of the concentration only. For the solute adsorption phenomenon it is the concentration at the membrane (c_w) that is of vital importance and thereby the resistance of the adsorption layer, i.e. $R_A = f(c_w)$. From equation 2 and 3 above we get

$$J_V = \frac{1}{R_M + R_A} (\Delta P - \sigma \pi) \quad (4)$$

the above equation can be written as

$$J_V = \frac{RF}{R_M} (\Delta P - \sigma \pi)$$

Dividing this equation by the flux of the pure buffer solution at the same applied pressure we get

$$J_V = J_O \frac{RF}{R_M} \left(1 - \frac{\sigma \pi}{\Delta P}\right) = J_A \left(1 - \frac{\sigma \pi}{\Delta P}\right) \quad (5)$$

In order to predict the transmembrane flux one must therefore know R_A or RF as a function of the concentration.

RESULTS AND DISCUSSION

The results from the measurements of the reduction in permeability for membranes that have been exposed to BSA protein solution are shown in figure 1. In this figure the relative flux reduction ($1 - RF$) is shown as a function of the concentration of the protein solution that has been in contact with the membrane.

As can be seen from these results, the reduction in flux for the hydrophobic polysulfone and polyamide membranes is much higher than that for the hydrophilic cellulose acetate membrane. The exposure to high protein concentration has a similar effect on the permeate flux of the two hydrophobic membranes. In both cases a semi-plateau is obtained around 0.4% BSA concentration. The relative flux reduction at this plateau is about 35%. Above this concentration the hydraulic resistance increases quite slowly up to BSA concentrations of approximately 20% for the polysulfone membrane and 30% for the polyamide membrane. Higher up in concentration the flux reduction has an exponential behaviour and close to 50% BSA concentration it is 75-80%.

The reduction in permeability of the hydrophilic cellulose acetate membrane has also reached a plateau value at low BSA concentration. The flux reduction is however much lower (around 10%). Unlike the two hydrophobic membranes no further changes in flux is observed at higher concentrations.

It is clear from the results in figure 1 that the resistance due to the adsorbed layer, R_A , is of the same order of magnitude as the membrane resistance, R_M . This means that R_A in equation 4 can not be neglected as this would cause a serious error in predicting the transmembrane flux. The experimental values in figure 1 can be fitted empirically by an equation of the form;

$$1 - RF = A + B_1 e^{r_1 c} + B_2 e^{r_2 c} \quad (6)$$

where A , B_1 , B_2 , r_1 and r_2 are experimentally determined parameters

c = protein concentration

or

$$RF = A_1 - B_1 e^{r_1 C} - B_2 e^{r_2 C} \quad (7)$$

where $A_1 = 1 - A$

Equation 6 combines two equations both of the form $A + B e^{rC}$ where the first one stands for the reduction in flux up to the plateau value while the second stands for the exponential increases at higher concentrations. The constant A represents the plateau value.

Regression analysis of the experimental results shown in figure 1 were done for the two equations that give equation 6. The results are shown in Table II.

Table II.

Membrane	Eq. I: $A + B_1 e^{r_1 C}$				Eq. II: $A + B_2 e^{r_2 C}$		
	A	B_1	r_1	correlation coeff.	B_2	r_2	correlation coeff.
I	0.350	-0.391	-10.91	0.98	0.54×10^{-3}	0.138	0.87
II	0.347	-0.306	-11.64	0.92	9.2×10^{-3}	0.078	0.92
III	0.096	-0.084	-1.04	0.70	0	-----	----

It can be seen from the regression analyses that the last term or B in equation 6 is zero for the cellulose acetate membrane as a consequence that no exponential increase in flux reduction is observed at high concentrations. The solid curves in figure 1 represents the results of the regression.

The empirical expression for the relative flux RF in equation 7 can be put into equation 5 to give

$$J_v = J_o (A_1 - B_1 e^{r_1 C} - B_2 e^{r_2 C}) \left(1 - \frac{\sigma \pi}{\Delta P}\right) \quad (8)$$

This equation which is valid in the pre-gel region takes into account the reduction in hydraulic permeability due to the protein layer formed and is therefore more elaborated than equation 2. The protein concentration c in equation 8 is that at the solid/liquid interface.

The results from the measurements of ^{14}C -labelled BSA that adsorb or coagulate on the membrane surface are shown in figure 2 and 3.

Figure 2 shows the isotherm for adsorption of BSA on the hydrophilic cellulose acetate membrane. These results agree well with the results of the hydraulic permeability measurements in figure 1. The maximum amount adsorbed is little above 2 mg BSA/m^2 which approximately corresponds to a monomolecular protein layer.

The same type of graphs for the polysulfone and polyamide membranes in figure 3 are quite different. The amount BSA that is bound to the membranes is considerably higher. In this case we have multimolecular layers of the protein so one can no longer talk about true adsorption phenomena but rather some kind of a surface attachment process.

It is rather unexpected that such a high amount of the BSA proteins coagulates on the two hydrophobic membranes. This indicates that the so called gel layer is not suddenly formed when the concentration reaches the solubility limit of the macrosolute but rather gradually formed as the surface concentration increases.

When comparing the results in figure 3 with the permeability results in figure 1, there are as expected a lot of similarities. In both cases a semi-plateau value is obtained around 0.4% BSA concentration. Just before 20% for the polysulfone and 30% for the polyamide membrane both the hydraulic resistance and the amount of BSA bound to the membranes start to increase more rapidly.

The reason for this sudden increase in the amount of protein that coagulates at higher concentration is unclear. The fact that protein tends to aggregate in solutions at higher concentrations is one of the factors that could contribute to the increase in surface binding. It is interesting to notice that the hydrophilic cellulose acetate membrane does not bind more protein at higher concentrations. It seems that after the adsorption of the monomolecular protein layer the surface characteristic is of such nature that no more protein or protein aggregates can stick to it.

The relative resistance of the protein layer R_M/R_A which can be expressed in the form $1/RF - 1$ can be calculated from the curves that fits the experimental results in figure 1. In figure 4 this relative resistance is plotted as a function of the amount of BSA that has bound to the two hydrophobic membranes according to the curves in figure 3.

It can be seen from figure 4 that a linear relationship exists up to 10 to 20 mg BSA/m² where there is a sharp brakepoint in the curve. Above this brakepoint there is another linear relationship up to about 300 mg BSA/m². After this the curve takes an exponential form.

From the slope of the curve it can be seen that the hydraulic resistance is highest for the first layer of 10-20 mg BSA/m² that is formed on the membrane surface. The protein layer between 10-300 mg BSA/m² has a very low hydraulic resistance. This layer is followed by a protein layer that has an increasing hydraulic resistance. These variations in density or permeability of the protein layer shows that the surface coagulation process is highly depending on the solute concentration of the protein. The sharp increase in the hydraulic resistance between 400 and 1000 mg/m² is remarkable and indicate that considerable reduction in permeability takes place in the immediate vicinity of the gel concentration.

REFERENCES

1. Blatt, W.F., Dravid, A., Michaels, A.S. and Nelsen, L. Solute polarization and cake formation in membrane ultrafiltration: Causes consequences and control techniques, Membrane Science and Technology, Plenum Press, New York, 1970, p 47-97.
2. Probststein, J.R.F., Shen, J.S. and Leung, W.F. Ultrafiltration of macromolecular solutions at high polarization in laminar channel flow. Desalination 24, 1978, 1-16.
3. Trettin, D.R. and Doshi, M.R. Limiting flux in ultrafiltration of macromolecular solutions. Chem. Eng. Commun. 4, 1979, 507-522.
4. Kozinski, A.A. and Lightfoot, E.N. Protein ultrafiltration: A general example of boundary layer filtration. AIChE. J. 18, (Nov), 1972, 1030-1040.
5. Goldsmith, R.L. Macromolecular ultrafiltration with microporous membranes. Ind. Chem. Fundam. 10, 1, 1971, 113-120.
6. Vilker, V.L., Colton, C.K. and Smith, K.A. Concentration polarization in protein ultrafiltration, II. Theoretical and experimental study of albumin ultrafiltered in an unstirred cell. AIChE. J. 27(4) 1981, 637-645.
7. López-Leiva, M. and Matthiasson, E. Solute adsorption as a source of fouling in ultrafiltration. Proc. from the International Workshop on the Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing. Tylösand, Sweden, 1981, 299-308.
8. Matthiasson, E. The role of macromolecular adsorption in fouling of ultrafiltration membranes. J. Membrane Sci. accepted 1982.

9. Busby, T.F. and Ingham, K.C. Separation of macromolecules by ultrafiltration: Removal of poly(ethylene glycol) from human albumin. *J. Biochem. Biophys. Methods.* 2, 1980, 191-206.
10. Michaels, A.S. and Lange, K.E. A study of solvent and macrosolute transport mechanisms in asymmetric ultrafiltration membranes. OWRT Contract No. 14.34.0001-8548, Stanford University, Department of Chemical Engineering, Report dated February 28, 1981.
11. Howell, J.A. and Velicangil, O. Theoretical considerations of membrane fouling and its treatment with immobilized enzymes for protein ultrafiltration. *J. Applied Polym. Sci.* 27, 1982, 21-32.
12. Norde, W. Proteins at interfaces. Ph.D. Thesis, Wageningen University, The Netherlands, 1976.
13. MacRitchie, F. The adsorption of proteins at the solid/liquid interface. *J. Colloid Interface Sci.* 38, 2, 1972, 484-488.
14. Dottavio-Martin, D. and Ravel, J.M. Radiolabeling of proteins by reductive alkylation with (^{14}C) formaldehyde and sodium cyanoborohydride, *Anal. Biochem.* 87, 1978, 562-565.

FIGURE LEGENDS

- Figure 1. Influence of the BSA concentration on the reduction in relative flux (1-RF) of a pure saline water solution (0.15 M NaCl, pH 7.0 and 25°C).
- Figure 2. Adsorption isotherms for BSA on membrane III (CA).
- Figure 3. Influence of the BSA concentration on the amount of BSA that coagulates on the polysulfone and polyamide membranes.
- Figure 4. Relative resistance of the BSA protein layer versus the amount that has bound to the membranes.

Fig. 1

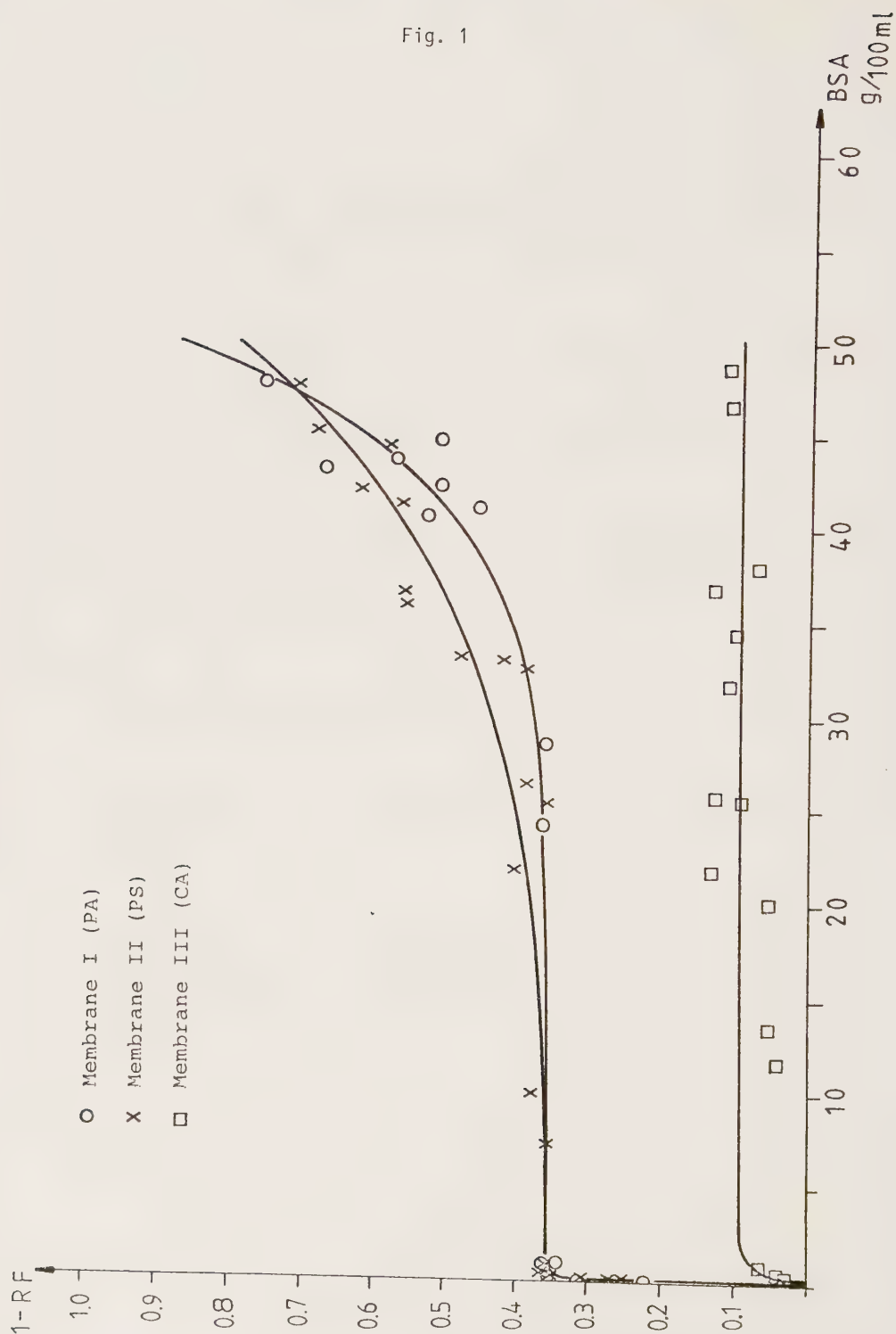


Fig. 2

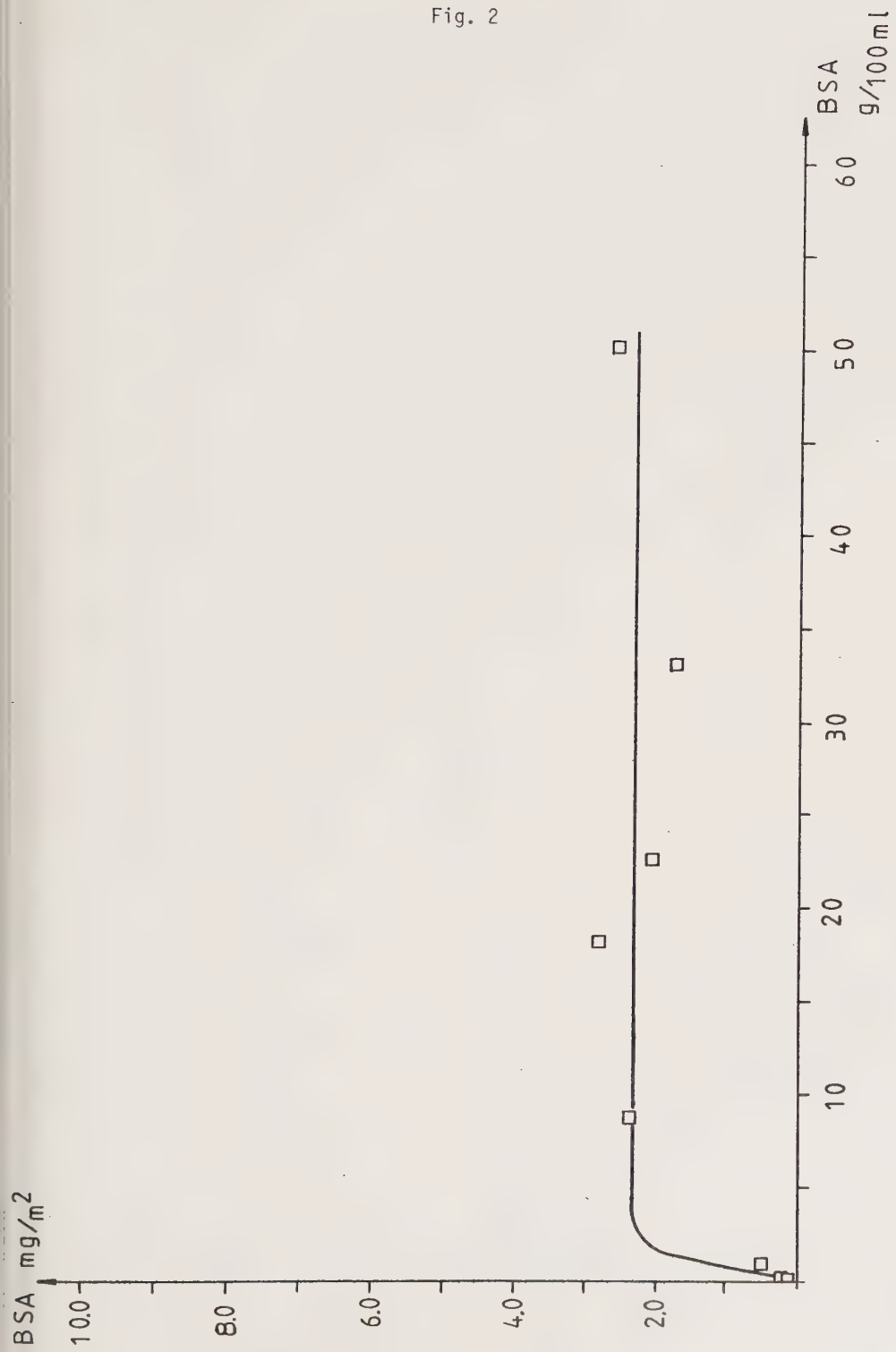
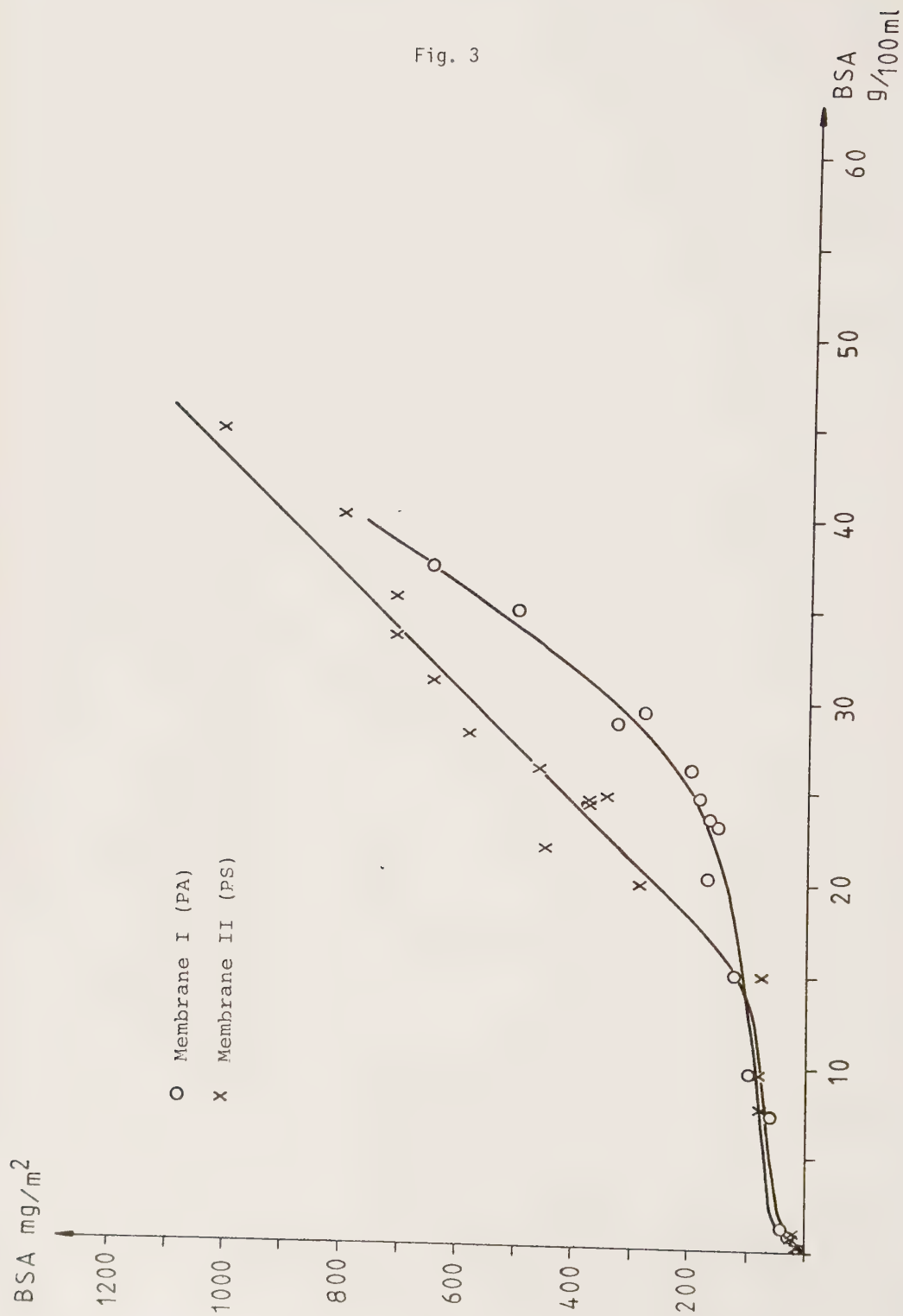


Fig. 3



1/R_F

1.5

1.0

0.5

Membrane II (PS)

Membrane I (PA)

Fig. 4

BSA
mg/m²

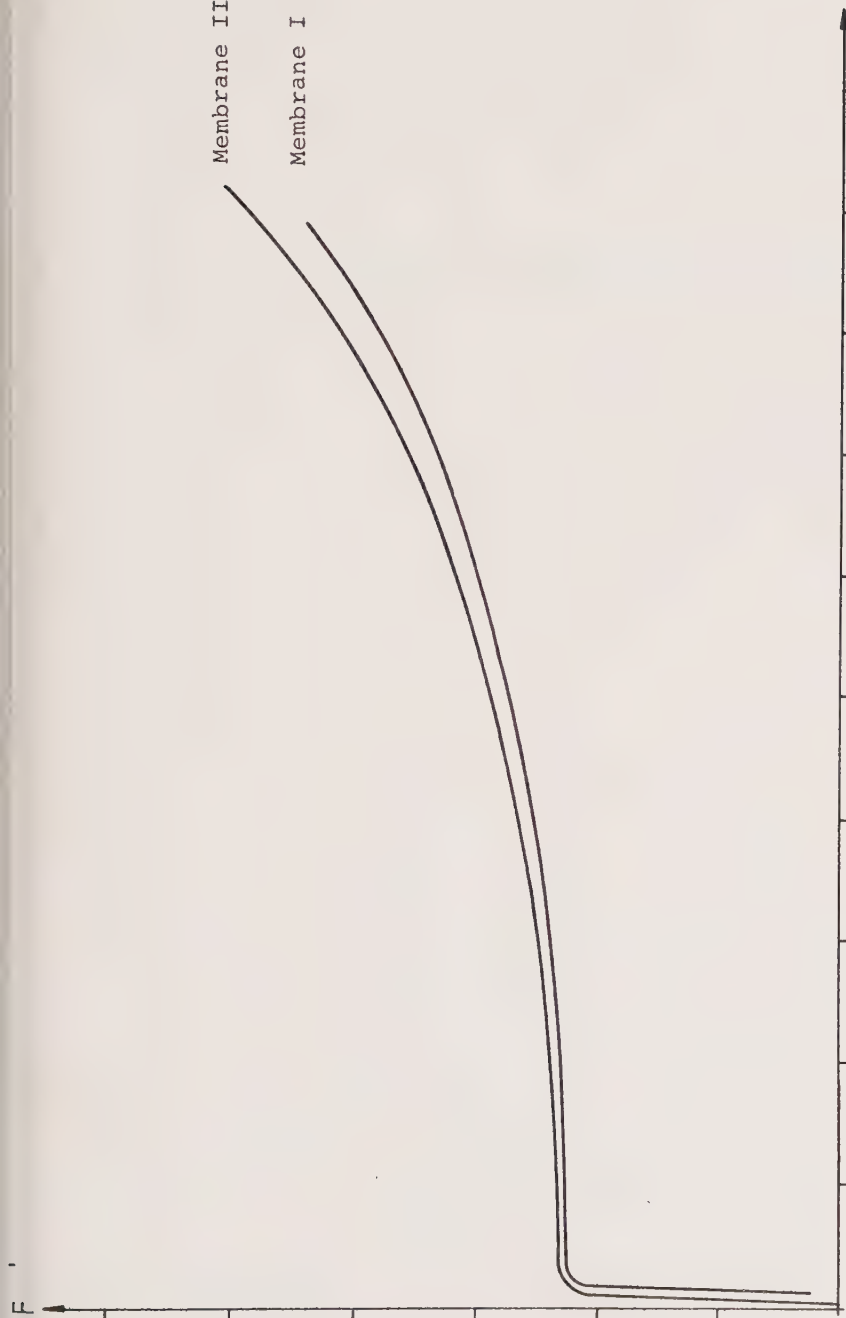
1000

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600

400

200



V

PREDICTION OF CONCENTRATION PROFILES
IN AN UNSTIRRED ULTRAFILTRATION BATCH CELL

By E. Matthiasson

PREDICTION OF CONCENTRATION PROFILES IN AN UNSTIRRED ULTRA-FILTRATION BATCH CELL.

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Summary

Concentration profiles in ultrafiltration of macromolecular solutions in an unstirred batch cell were predicted by means of numerical calculation of the unsteady state one dimensional convective diffusion equation. The calculations were done for bovine serum albumin (BSA) with both variable and constant diffusivity data from the literature. The concentration dependency of the density was taken into account. The results were compared with previous studies on the hydraulic resistance of the adsorption layer and physical data of the osmotic pressure of the solute. Reasonable good agreement with experimental data was found when permeate fluxes were predicted by means of a semiempirical equation developed in previous studies.

Introduction

Ultrafiltration is a well known unit operation for separation and concentration of macromolecular solutions. One of the factors that often impedes or limits the use of this unit operations is the fouling of the membrane. In previous studies (1,2) has been shown that adsorption of proteins on the membrane surface plays an important role in the fouling process and that it causes a considerable decrease in the hydraulic permeability.

The flux behaviour in ultrafiltration is usually described by theories stating that it either depends on the gel layer resistance and back-diffusion of solute (3,4) or the osmotic pressure of the solute (5,6). The unstirred batch cell has been found useful by many investigations when studying the fundamental principles of ultrafiltration.

Trettin and Doshi (7) used this system to study the ultrafiltration of bovine serum albumin (BSA). They found that the permeate flux could be predicted by an integral method solution of the mass balance equation assuming that a solute gel concentration is reached instantaneously at the membrane surface and a constant value of the diffusion coefficient. The fluxes were found to decay like $(\text{time})^{-\frac{1}{2}}$ for both the theoretical solution and experimental data. The film theory model on the other hand underpredicted the experimental flux measurements.

Vilker et al (8) using a regular perturbation theory obtained a theoretical solution which describes the flux and the concentration polarization phenomena during ultrafiltration.

The theoretical solution was found to be in agreement with experimental concentration profiles and ultrafiltration flux measurements of BSA solutions. Their conclusion was that the ultrafiltration flux is limited by the osmotic pressure of the solution.

Gernedel (9) used an unstirred batch cell system to study ultrafiltration of milk proteins. He found that the permeate flux through the membrane could be explained by a simple particle filtration model where the resistance was directly proportional to the amount of material deposited. The specific resistance was found to depend on the applied pressure which he explained by the compression of the deposited layer.

Recently Reihanen et al (10) studied the flux time behaviour in an unstirred batch cell. They used the technique of step-changes in pressure, previously used by Dejmek (11) in a stirred batch system, to find out which of the three models the gel layer polarization, the osmotic pressure or the particle filtration model is most valid. Their conclusion was that the particle filtration model was in best agreement with the experimental results.

The main objective of this work is to predict the concentration profiles in an unstirred batch cell from which the influence of the adsorption on the flux and the validity of an expression for the permeate flux derived in previous adsorption studies (1,2) can be determined. In this study, as in the previous ones, BSA has been chosen as a macrosolute.

Theory and problem statement

The mass fluxes in an unstirred batch cell ultrafiltration system are given by the unsteady state one-dimensional convective diffusion equation

$$\frac{\partial c}{\partial t} + \frac{\partial (cu)}{\partial y} = \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right) \quad (1)$$

where c is the concentration of solute, u is the transmembrane velocity, y is the distance normal to the membrane surface and D the solute diffusivity. In order to calculate the BSA concentration at the membrane surface and across the concentration boundary layer this equation has to be solved either analytically or numerically. If both the velocity and the diffusivity are assumed constant a close form solution can be obtained by using Laplace transformation (11). Other types of solutions can be obtained by making appropriate assumptions and by means of appropriate boundary conditions. One of the most common simplifications of equation 1 is the assumption of constant density and constant diffusivity. In this case the equation becomes

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial y} + D \frac{\partial^2 c}{\partial y^2} \quad (2)$$

The error caused by the assumption of constant density is easily estimated by density measurements. The validity of the assumption of constant diffusivity is on the other hand more difficult to confirm as it is rather complicated to perform diffusivity measurements and the experimental data found in the literature are quite limited. As experimental measurements on the diffusion coefficient of macromolecules (12,13) often show a strong dependency on concentration, this assumption of constant diffusivity could cause serious errors in the calculations.

In the case of non-linearities the only way to solve equation 1 is by a numerical method such as a finite difference method.

When solving the unsteady state one-dimensional convective diffusion equation the changes in the transmembrane velocity versus time can either be obtained from experimental data or from some other expressions for the flux. The permeate flux J_v can be given by the equation

$$J_v = L_p (\Delta P - \sigma \Delta \Pi) \quad (3)$$

where L_p is the hydraulic permeability, σ is the rejection coefficient, ΔP is the applied pressure and $\Delta \Pi$ is the difference in osmotic pressure at both sides of the membrane. Usually both the hydraulic permeability L_p and the osmotic pressure Π are dependent on solute concentration. If the concentration dependency of L_p and Π is known these expressions can be put into equation 3. In that case equation 3 gives the flux J_v as a function of the concentration alone.

Previous adsorption studies

In previous studies (1,2) we have shown that proteins adsorb spontaneously on the membrane surface. This adsorption can cause as much as 35% reduction in the permeate flux when the wall concentration is below 1%. Over 1% sometimes the flux decreases gradually with increasing concentration to become as low as 20-35% of the original value at 50% wall concentration. The reduction in permeability caused by this adsorption was expressed (2) by the empirical equation

$$1 - RF = A + B_1 e^{r_1 c} + B_2 e^{r_2 c} \quad (4)$$

RF is the relative flux equal to J_A/J_O where J_O and J_A are the flux of pure buffer solution before and after adsorption. A , B_1 , B_2 , r_1 and r_2 are experimentally determined parameters, c is the protein concentration that has been in contact with the membrane surface.

The permeate flux in ultrafiltration, J_v can be expressed by equation 3 where the hydraulic permeability is given as

$$L_p = \frac{1}{R_M + R_A}$$

R_M is the resistance of the membrane and R_A the resistance of the adsorbed layer. Equation 3 can be rewritten (2) as

$$J_v = J_{O RF} \left(1 - \frac{\sigma \Delta \Pi}{\Delta P}\right) = J_A \left(1 - \frac{\sigma \Delta \Pi}{\Delta P}\right) \quad (5)$$

The relative flux in this equation can be obtained from equation 4. In this case it is assumed that the adsorption takes place immediately. This is a reasonable assumption since it has been found (14) that the kinetic of the adsorption is primarily diffusion controlled and in ultrafiltration the diffusion to the surface is replaced by the convective flow.

Materials and Methods

Ultrafiltration experiments with bovine serum albumin (BSA, 0.1-1%) were performed in an unstirred ultrafiltration batch cell. The BSA protein used were purchased from Sigma Chemical Company, product no A 7511. Every protein solution was made in 0.15 M NaCl at pH 7.0. The water used in the solutions was prefiltered through a ultrafiltration membrane with a cut off of 1 000 daltons after distillation and deionization.

Cellulose acetate and polysulfone membranes (cut off 20 000) manufactured by the Danish Sugar Corporation, Denmark and a polyamide membrane (cut off 10 000) manufactured by Berghof GmbH, F.R.G. were used in the experiments.

The batch ultrafiltration experiments were done in a standard circular ultrafiltration batch cell with an effective membrane area of 4 cm². The cell was thermostated in a water bath and pressurized with nitrogen through a reservoir filled with BSA solution. The solution passed through a 0.22 µm filter before entering the cell. The flux was measured with an electronic balance connected to a microcomputer that collected the data.

Density measurements for BSA concentrations up to 45g/100 ml in 0.15M NaCl solution at pH 7.0 and 25°C were done with a pycnometer.

The osmotic pressure of BSA solutions

The experimental data available in the literature on the osmotic pressure of BSA and other protein solutions deal primarily with low concentrations. Measurements on BSA at high concentration are quite limited and disagree to some extent.

Scatchard et al (15,16) measured the osmotic pressure of BSA solutions for concentrations up to 25% at pH from 4.2 to 8.2 and molar salt concentrations from 0.05 to 0.20. The osmotic pressure was represented by the equation

$$P = 2.68 c (1 + B_2 c) \quad (6)$$

where P is the pressure in mm Hg at 0°C , c is the concentration of solute and B_2 is a pH and concentration depending parameter that can be expressed for pH 5.4 to 7.4 by the equation

$$B_2 = (417 - 24.5 Z) (1 + 0.02 c) \cdot 10^{-4}$$

Z is the molecular charge of the protein. This expression for the osmotic pressure for pH 7 is plotted in figure 1.

Vilker et al (17) measured the osmotic pressure of BSA at 25°C in 0.15 M NaCl at pH 4.5, 5.4 and 7.4 for concentrations between 8 and 48%. These experiments were performed in an osmometer cell consisting of two chambers where a pressure equal to the osmotic pressure is applied to the saline solvent side. The results were described by a semiempirical equation (see figure 1)

$$\Pi = RT \left\{ 2 \left[\left(\frac{Z_1 c_p}{2 M_p} \right)^2 + m_s \right]^{\frac{1}{2}} - 2 m_s \right\} + \frac{RT}{M_p} \left(c_p + A_2 c_p^2 + A_3 c_p^3 \right) \quad (7)$$

Π is the osmotic pressure, M_p is the molecular weight of the protein, m_s is molar salt concentration, c_p is BSA concentration in g/l, R and T have their usual meanings and A_2 and A_3 are pH depending parameters given by the equations

$$A_2 = - 5.625 \times 10^{-4} - 2.410 \times 10^{-4} Z_1 - 3.664 \times 10^{-5} Z_1^2$$

$$A_3 = - 2.950 \times 10^{-5} - 1.05 \times 10^{-6} Z_1 - 1.762 \times 10^{-7} Z_1^2$$

where Z_1 is the macro-ion charge number. The first term in the semiempirical equation accounts for ideal Donnan effect and the second term accounts for nonidealities due to interaction in the solution.

It is obvious from figure 1 that the results of Scatchard et al and Vilker et al disagree quite markedly. According to the results of Vilker et al the osmotic pressure depends much more strongly on the concentration for the BSA solution above 12% concentration. The reason for these disagreements is unclear. Scatchard et al observed in their experiments that different types of BSA preparations gave different osmotic pressures at the same concentration. This difference was between 4 and 5% at 6 g/100 ml concentration of the BSA solution. It is not possible to predict what the difference in osmotic pressure for these two samples would be at higher concentration but this indicates that one can expect some differences for protein solutions from different manufactures.

The diffusion coefficient

In order to solve equation 1 the macromolecular diffusivity of BSA as a function of the solute concentration has to be known. Unfortunately, available data on the diffusion coefficient are quite rare. Most of the experimental data found in the literature are for diluted solutions (18,19) which can not be extrapolated to the high concentrations found in the concentration polarization layer.

Keller et al (12) measured the diffusivity of BSA at the isoelectric point (pH 4.7) for concentrations between 1 and 30 g/100 ml in 0.1 M acetate buffer. They found that the diffusivity data at this pH can be described by the equation

$$D = D_0 \tanh(\alpha\phi)/\alpha\phi \quad (8)$$

where D_0 is the diffusivity at infinite dilution, α is an empirical parameter (21.3 for serum albumin) and ϕ is the volume fraction of the solute.

The mutual diffusion coefficient of species in dilute solutions can be expressed by the Stoke-Einstein equation

$$D = K_b \cdot T/f \quad (9)$$

where K_b is Boltzmann's constant, T the absolute temperature and f is the drag coefficient of the solute. Doherty and Benedek (19) showed that electrostatic interactions between the protein molecules and counterions in solution can play a part in the diffusion process.

Phillies (21) pointed out that at high protein concentration solute-solute interactions contribute to the mutual diffusion coefficient and if the molecules interact repulsively the diffusivity increases. The diffusion coefficient in presence of such interactions is given by the generalized Stoke-Einstein relation

$$D = \frac{(\partial \Pi / \partial c)_{P,T}}{f} (1-\Phi) \quad (10)$$

where $(\partial \Pi / \partial c)_{P,T}$ is the isothermal osmotic compressibility of the solute and f and Φ are the same as before. The drag coefficient f can be obtained from equation 9.

Phillies et al (13) measured the diffusion coefficient of BSA by using quasielastic light scattering spectroscopy over the pH range 4.3 to 7.6 for concentrations up to 33%. They found the results to prove the validity of equation 10 above. Figure 2 shows the results from their measurements of BSA in 0.15 M NaCl solution at pH 7.2-7.3. The solid line shows the prediction of the generalized Stoke-Einstein equation at pH 7 for $(\partial \Pi / \partial c)_{P,T}$ values from the measurements of Scatchard et al and the drag coefficient f from the tracer measurements of Keller et al. The results of Phillies et al around pH 4.7 gave diffusion coefficients that were close to $6 \times 10^{-11} \text{ m}^2/\text{s}$ and the diffusivity was found to be a relatively weak function of concentration up to at least 20% concentration. These results are in complete disagreements with the results by Keller et al where the diffusivity was found to decrease strongly with increasing concentration.

Shen and Probstein (22) calculated the diffusivity at the gel concentration from ultrafiltration experimental data, by using their expression for the limiting flux in parallel plate geometry

$$J_{Wlim} = k \left(\frac{U \cdot D_g^2}{h \cdot L} \right)^{1/3} \cdot \ln \frac{c_g}{c_b} \quad (11)$$

where J_{Wlim} is the limiting flux, U is the mean bulk flow velocity, D_g is the diffusion coefficient at the gel concentration, h is the channel half-width, L is active membrane length, k is a constant, c_g and c_b are the gel- and bulk concentration respectively. At pH 7.4 they found that the diffusion coefficient at the gel concentration (58%) was around $6.7 \times 10^{-11} \text{ m}^2/\text{s}$.

Probstein et al (23) used the same method to determine the diffusivity at the gel concentration at pH 4.7. The gel concentration at this pH was found to be 34% and the diffusivity obtained from the equation above was $5.6 \times 10^{-11} \text{ m}^2/\text{s}$. This value is in agreement with the measurements of Phillies et al but four times higher than the value of $1.4 \times 10^{-11} \text{ m}^2/\text{s}$ obtained by Keller et al.

In figure 2 a curve fit by a least square regression analysis to a 5th order equation is presented to the experimental data of Phillies et al and the calculated diffusivity of Shen and Probstein.

Numerical solution

As it has been stated before equation 1 can be solved either numerically or analytically. In this paper numerical solutions are presented using a so called control volume discretization formulation (24).

Equation 1 can be rewritten in the form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} - cu \right) \quad (12)$$

Assuming constant concentration in each control volume the discretization equation for the left hand side of equation 12 is given in the form

$$\int_w^e \int_t^{t+\Delta t} \frac{\partial c}{\partial t} dt dy = \Delta y_p (c_p - c_p^o) \quad (13)$$

where the subscript p is for the middle point of the control volume P and the superscript o stands for the previous time value of c, Δy_p is the length of the control volume.

Using an implicit scheme to give the variation in c with y (24,25) the discretization equation for the right hand side of equation 12 is given as

$$\begin{aligned} \int_t^{t+\Delta t} \int_w^e \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} - cu \right) dy dt = & \left[f \left(D_e \frac{c_E - c_p}{\partial y_e} - D_w \frac{c_p - c_w}{\partial y_w} \right. \right. \\ & - \frac{1}{2} \cdot \left(u_e (c_E + c_p) - u_w (c_p + c_w) \right) \left. \right) + (1-f) \left(D_e^o \frac{c_E^o - c_p^o}{\partial y_e} - \right. \\ & \left. \left. - D_w^o \frac{c_p^o - c_w^o}{\partial y_w} - \frac{1}{2} \left(u_e^o (c_E^o + c_p^o) - u_w^o (c_p^o + c_w^o) \right) \right) \right] \cdot \Delta t \quad (14) \end{aligned}$$

where f is given by the equation (25)

$$f = \frac{1}{1 - \exp(\lambda_p)} - \frac{1}{\lambda_p} \quad (15)$$

$$\lambda_p = \frac{\Delta t}{\Delta y_p} \left(\frac{D_e}{\partial y_e} + \frac{D_w}{\partial y_w} + \frac{u_e}{2} - \frac{u_w}{2} \right)$$

The exponential expression in the formulation of f (Equ. 15) is derived from the exact solution of the ordinary differential equation describing the time integration. It eliminates locally the truncation error which is otherwise obtained through a conventional Taylor series expansion.

Subscripts W and E indicate the value in the middle of the control volumes before and after the control volume p respectively, while w and e indicates the value at the boundary of the control volume. ∂y_w and ∂y_e is the distance between the grid points.

These discretization equations are given at every grid point and solved directly with a tridiagonal matrix algorithm.

The boundary and initial conditions used are the following

$$c(0,y) = c_o$$

$$c(t,\infty) = c_o$$

$$J_v \cdot c(t,0) + D(c) \cdot dc(t,0)/dy = (1-\sigma) \cdot J_v \cdot c(t,0)$$

The first equation gives the initial condition of uniform concentration in the whole system. The second one gives the boundary condition far away from the membrane surface where no changes in concentration are noticed. The third one gives the mass balance at the membrane surface. Changes in velocity due to density difference and accumulation of solute in the polarization layer were taken into account.

The solution obtained from the numerical calculation of equation 1 for constant velocity and constant diffusivity were compared with the exact analytical solution (11) in figure 3 showing good agreement for all time values considered.

Results and discussion

The results of the density measurements of the BSA solution can be represented by the following equation

$$\rho = 2.53 c + 1\ 000 \quad (12)$$

where the density ρ is in kg/m^3 and c the concentration of BSA in g/100 ml. This expression is in good agreement with the results of Vilker et al (8) and was used to compensate for the changes in velocity due to density differences.

The concentration profiles were calculated for concentration dependent diffusion coefficients according to both the prediction of the Stoke-Einstein equation and the curve fit of experimental data. Similar calculations were done for two constant diffusion coefficients (6.2×10^{-11} and $6.7 \times 10^{-11} \text{ m}^2/\text{s}$). Experimental data from the batch cell experiments were used to express the velocity.

Typical results of the wall concentration build-up versus time are plotted in figure 4. During first 30-40 sec the calculated concentration is almost equal for all four diffusion coefficients. In this time interval the diffusion back flux is very small compared to the transmembrane flux. After about 40 sec the curves start to differentiate. The concentration increases most rapidly during the first 300-400 sec whereon the curves bend off. The slopes of the curves are in inverse relation to the diffusion coefficient and as expected the lowest diffusivities give the highest wall concentration and vice versa.

Figure 5 shows the whole concentration profile for the experiment presented in figure 4 calculated for the diffusion coefficient that fits the experimental data. This figure reflects the results of figure 4. The concentration increases most rapidly in the beginning to reach the maximum wall concentration after about 2500 sec. The time needed to reach maximum concentration is of course highly depending on the bulk concentration and the transmembrane flux. Almost the whole concentration boundary layer is within a distance of 150μ from the membrane surface.

In figures 6 and 7 the reduction in flux (1-RF) is plotted versus wall concentration. It appears from these figures that the relation between the flux reduction and the calculated concentration is highly depending on the diffusivity. The Stoke-Einstein equation gives higher diffusion coefficients than the other expressions. As a consequence the wall concentration increases in this case more slowly and high flux reduction appears already at low concentrations. The bend of the curves at high concentration instead of the expected continuous exponential increase indicates that the diffusivity is overestimated at these concentrations.

It can be seen from the figures that the experimental flux reduction is already from the beginning higher than the reduction caused by the adsorbed layer alone. As the osmotic pressure of the BSA solutions is almost zero at low concentration the flux should be equal to J_{ORF} or J_A according to equation 5. This means that there is an additional resistance beside the one caused by the membrane itself and the adsorbed layer. It is not clear what is causing this flux reduction but one possible explanation could be some secondary "adsorption" layer that is only weakly bound. Accordingly this layer is more or less reversibly bound to the surface and therefore not detected in the adsorption resistance measurements with pure buffer solutions.

If this resistance is taken into account the hydraulic permeability in equation 3 should be rewritten as

$$L_p = \frac{1}{R_M + R_A + R_A'}$$

where R_A' corresponds to the secondary adsorption layer. This expression gives lower values for the relative flux RF or the flux after adsorption J_A in equation 5.

Figures 6 and 7 present the osmotic pressures as calculated from equation 5 and compare them with the measurements of Scatchard et al and Vilker et al. In these calculations the secondary hydraulic resistance was taken into account assuming that it caused the same reduction in flux in the whole concentration range. This second hydraulic resistance is shown by the dotted lines in the figures.

As it can be seen from these curves the values of the calculated osmotic pressure for constant diffusivity of $6.2 \times 10^{-11} \text{ m}^2/\text{s}$ fit best with the results of Scatchard et al. The experimentally fitted diffusion coefficient gives osmotic pressure values that are between the two predicted curves. The semiempirical diffusivity gives osmotic pressure values that are higher than both of them.

The high concentration dependency of the osmotic pressure given by Vilker et al is unrealistic for all the diffusion coefficients tested, expect those given by the semiempirical expression, since after a certain filtration time the predicted osmotic pressure exceeds the applied pressure.

In order to see how well equation 5 predicts the flux it was put into the unsteady state one-dimensional convective diffusion equation, which then was solved numerically as before. The flux according to equation 5 was obtained by iteration until convergence was obtained. The expression of Scatchard et al was used for the osmotic pressure term in equation 5. The relative flux term was obtained from equation 4 for which experimental parameters were known from previous studies (2). The effect of the secondary hydraulic resistance was taken into account in the same way as in the osmotic pressure calculations. The numerical calculations were done for constant diffusivity of $6.2 \times 10^{-11} \text{ m}^2/\text{s}$ and for the semiempirical and experimentally fitted diffusion coefficients.

Figure 8 and 9 show three different predictions which are compared to the experimental data from unstirred batch cell ultrafiltration with polyamide and cellulose acetate membranes as well as a polysulfone membrane that previously had been exposed to 43% BSA solution.

These results show that when the two expressions for the concentration dependent diffusivity are used the flux is overestimated. This means that the diffusion coefficient is too high and as a consequence the predicted wall concentration too low. The prediction of the flux from equation 5 fits best when the diffusivity is taken to be $6.2 \times 10^{-11} \text{ m}^2/\text{s}$. In this case the flux is slightly overestimated in the beginning. The cause of this could to some extent be explained by too low osmotic pressure values given by Scatchard et al as indicated in figures 7 and 8. At longer times in the last part of the curves the flux is on the other hand little underestimated. This is expected as the diffusivity, according to the theoretical prediction, increase to some extent at higher concentrations. The constant diffusivity assumed is therefore too low in this region which result in too high wall concentration.

Conclusion

The results from the numerical calculations show that the concentration profile are highly depending on the diffusion coefficient. Studies of the flux reduction and the hydraulic resistance of the adsorbed layer indicate that there is some additional resistance which is not as tightly bound to the surface as the adsorbed layer. Predictions of the flux with equation 5 where the concentration dependency of the hydraulic resistance is taken into account show reasonable good agreement for constant diffusion coefficient of $6.2 \times 10^{-11} \text{ m}^2/\text{s}$ and the osmotic pressure values given by Scatchard et al.

REFERENCES

1. E. Matthiasson. The Role Macromolecular Adsorption in Fouling of Ultrafiltration Membranes. J. Membrane Sci., 16 (1983) 23-36.
2. E. Matthiasson, B. Hallström and B. Sivik. Adsorption Phenomena in Fouling UF-Membranes, in: B. McKenna (Ed), Engineering and Food, Volume 1, Proc. from the Third International Congress on Engineering and Food, Dublin, Ireland (1983).
3. W.F. Blatt, A. Dravid, A.S. Michaels and L. Nelson. Solute Polarization and Cake Formation in Membrane Ultrafiltration: Causes Consequences and Control Techniques, Membrane Science and Technology, Plenum Press, New York, (1970) 47-97.
4. J.R.F. Probst, J.S. Shen and W.F. Leung. Ultrafiltration of Macromolecular Solutions at High Polarization in Laminar Channel Flow. Desalination 24, (1978) 1-16.
5. A.A. Kozinski and E.N. Lightfoot. Protein Ultrafiltration: A General Example of Boundary Layer Filtration. AIChE. J. 18 (1972) 1030-1040.
6. R.L. Goldsmith. Macromolecular Ultrafiltration with Microporous Membranes. Ind. Chem. Fundam. 10 (1971) 113-120.
7. D.R. Trettin and M.R. Doshi. Ultrafiltration in an Unstirred Batch Cell, Ind. Eng. Chem Fundam 19, (1980) 189-194.
8. V.L. Vilker, C.K. Colton and K.A. Smith. Concentration Polarization in Protein Ultrafiltration, II, Theoretical and Experimental Study of Albumin Ultrafiltered in an Unstirred Cell. AIChE 27 (4) (1981) 637-645.
9. G. Gernedel. Über die Ultrafiltration von Milk und die den Widerstand der Ablagerungsschicht beeinflussenden Faktoren. Ph.D. thesis, Technischen Universität München (1980).

10. H. Reihanian, C.R. Robertson and A.S. Michaels. Mechanism of Polarization and Fouling of Ultrafiltration Membranes by Proteins, *J. Membrane Sci.*, 16 (1983) 237-258.
11. P. Dejmek. Concentration Polarization in Ultrafiltration of Macromolecules, Ph.D. thesis, Lund University (1975).
12. K.H. Keller, E.R. Canales and S.I. Yum. Tracer and Mutual Diffusion Coefficient of Proteins, *J. Phys. Chem.* 75 (1971) 379-387.
13. G.D.J. Phillies, G.B. Benedek and N.A. Mazer. Diffusion in Protein Solutions at High Concentration. A Study by Quasielastic Light Scattering Spectroscopy, *J. Chem. Phys.* 65 (1976) 1883-1892.
14. E. Matthiasson. Macromolecular adsorption and fouling in ultrafiltration and their relationships to concentration polarization, Ph.D. thesis, Lund University (1984).
15. G. Scatchard, A.C. Batchelder and A. Brown. Preparation and Properties of Serum and Plasma Proteins. VI. Osmotic Equilibria in Solutions of Serum Albumin and Sodium Chloride. *J. Amer. Chem. Soc.* 68 (1946) 2320-2329.
16. G. Scatchard, A.C. Batchelder, A. Brown and M. Zosa. Preparation and Properties of Serum and Plasma Proteins. VII. Osmotic Equilibria in Concentrated Solutions of Serum Albumin. *J. Amer. Chem. Soc.* 68 (1946) 2610-2612.
17. V.L. Vilker, C.K. Colton and K.A. Smith. The Osmotic Pressure of Concentrated Protein: Effect of Concentration and pH in Saline Solutions of Bovine Serum Albumin, *J. Colloid Interface Sci.* 79 (1981) 548-566.
18. J.M. Creeth, The Use of the Gouy Diffusiometer with Dilute Protein Solutions. An assessment of the Accuracy of the Method, *Biochem.* 51 (1952) 10-17.

19. P.A. Charlwood. Estimation of Heterogeneity from Diffusion Measurements, J. Phys. Chem. 57 (1953) 125.
20. D. Doherty and G.B. Benedek. The Effect of Electric Charge on the Diffusion of Macromolecules, J. Chem. Phys. 61 (1974) 5426-5434.
21. G.D.J. Phillis. Effect of Intermacromolecular Interactions on Diffusion. I. Two-component solutions, J. Chem. Phys. 60 (1974) 976-982.
22. J.J.S. Shen and R.F. Probstein. On the Prediction of Limiting Flux in Laminar Ultrafiltration of Macromolecular Solutions, Ind. Eng. Chem. Fundam. 16 (1977) 459-465.
23. R.F. Probstein, W.F. Leung and Y. Alliance. Determination of Diffusivity and Gel Concentration in Macromolecular Solutions by Ultrafiltration. J. Phys. Chem 83 (1979) 1228-1232.
24. S.V. Patankar. Numerical Heat Transfer and Fluid Flow, Washington (1980).
25. S.V. Patankar, B.R. Baliga. A new finite-difference scheme for parabolic differential equations. Numerical Heat Transfer 1:27 (1978).

Figure Legends

- Figure 1 The osmotic pressure as a function of BSA concentration in 0.15 M NaCl at pH 7 and 25°C.
a) Results of Vilker et al (equation 7)
b) Results of Schatchard et al (equation 6)
- Figure 2 The diffusion coefficient of BSA in 0.15 M NaCl at 25°C as a function of concentration. Experimental data of Phillis et al, + pH 7.2 - 7.3, □ pH 7.4. Result of Shen and Probstein, Δ pH 7.4. The solid lines indicates
a) the prediction of the generalized Stokes-Einstein equation (pH 7) b) Curve fit of experimental data.
- Figure 3 Concentration profiles in an unstirred batch cell ultrafiltration of a 0.1% solution at constant transmembrane velocity (1×10^{-4} m/s) and constant diffusivity (6×10^{-11} m²/s) calculated by an exact close from Laplace solution ———, and the numerical calculation -----.
- Figure 4 Calculated wall concentrations and flux versus time in an unstirred batch cell ultrafiltration of 0.1% BSA solution 0.1 MPa through a polyamide membrane for different diffusivities: a) 6.2×10^{-11} m²/s, b) 6.7×10^{-11} m²/s, c) Variable according to the fit of experimental data, d) Variable according to the prediction of the generalized Stoke-Einstein equation.
The flux is given by e).
- Figure 5 Concentration profiles calculated for the experimentally fitted diffusivity (same experiment as in figure 4).
- Figure 6 and 7 The relative flux reduction ($1 - J_v/J_o$) and the osmotic pressure predicted by equation 5 versus calculated wall concentration in ultrafiltration of a 0.1% BSA solution (Figure 6 polyamide membrane 0.1 MPa and figure 7 cellulose acetate membrane 0.25 MPa) for different diffusivi-

ties; — - — - according to the semiempirical Stoke-Einstein equation, - · - · - experimental fitted diffusivity, ---- $D = 6.2 \times 10^{-11} \text{ m}^2/\text{s}$. The solid lines indicates a) flux reduction caused by the adsorbed layer b) Prediction of Π by Vilker et al, c) Prediction of Π by Scatchard et al.

The dotted line parallel to line a) indicates the reduction due to hydraulic resistance when the secondary resistance R_A' is taken into account.

Figure 8 and 9 Permeate flux versus time in ultrafiltration of 0.1% BSA solution. Figure 8 Polyamide membrane 0.1 MPa. Figure 9 a) cellulose acetate membrane 0.25 MPa and b) polysulfone membrane 0.10 MPa previously exposed to 43% BSA solution. The solid lines indicate experimental data and the other predictions according to equations for three diffusivities, — - — - — according to the Stoke-Einstein equation, - · - · - experimentally fitted diffusivity, ---- $D = 6.2 \times 10^{-11} \text{ m}^2/\text{s}$.

Fig. 1.

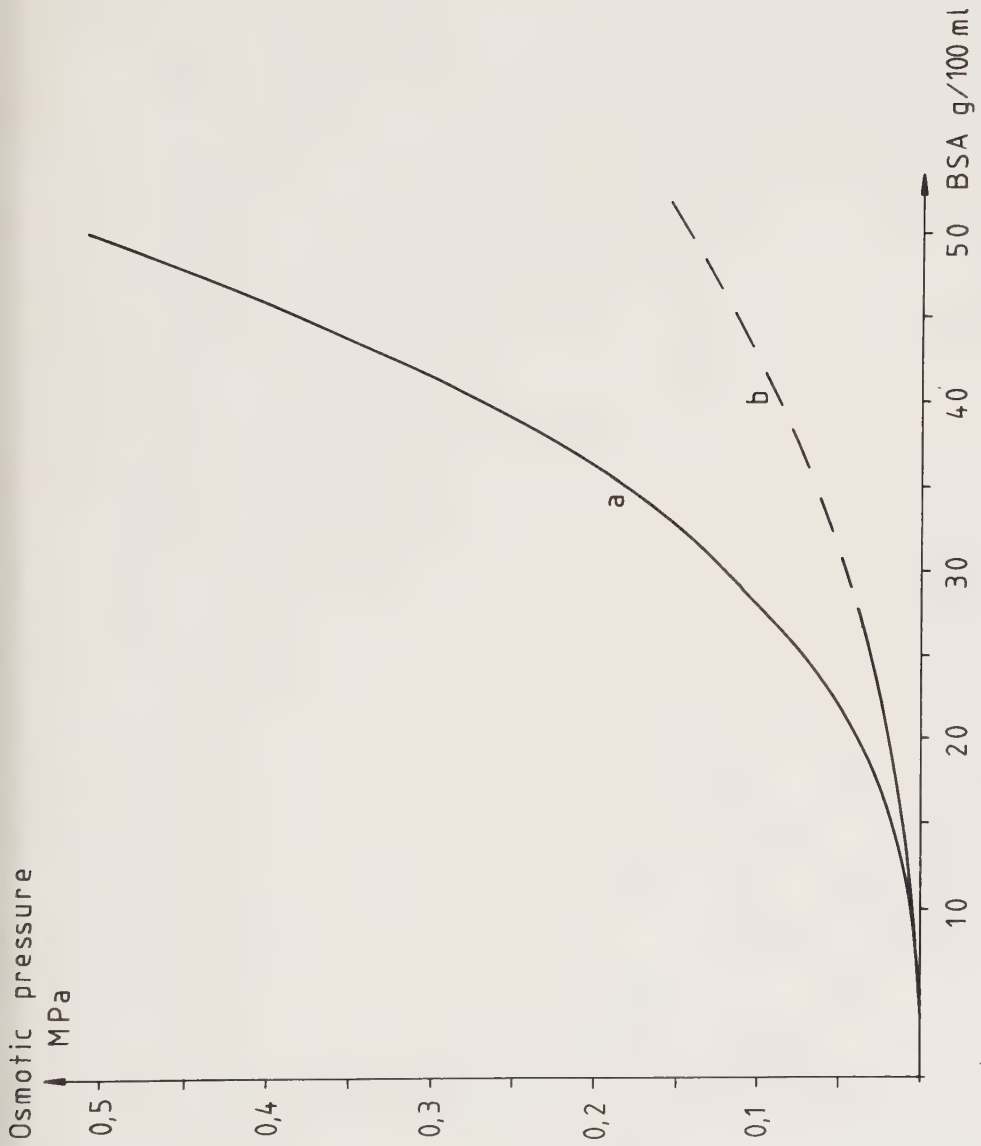


Fig. 2.

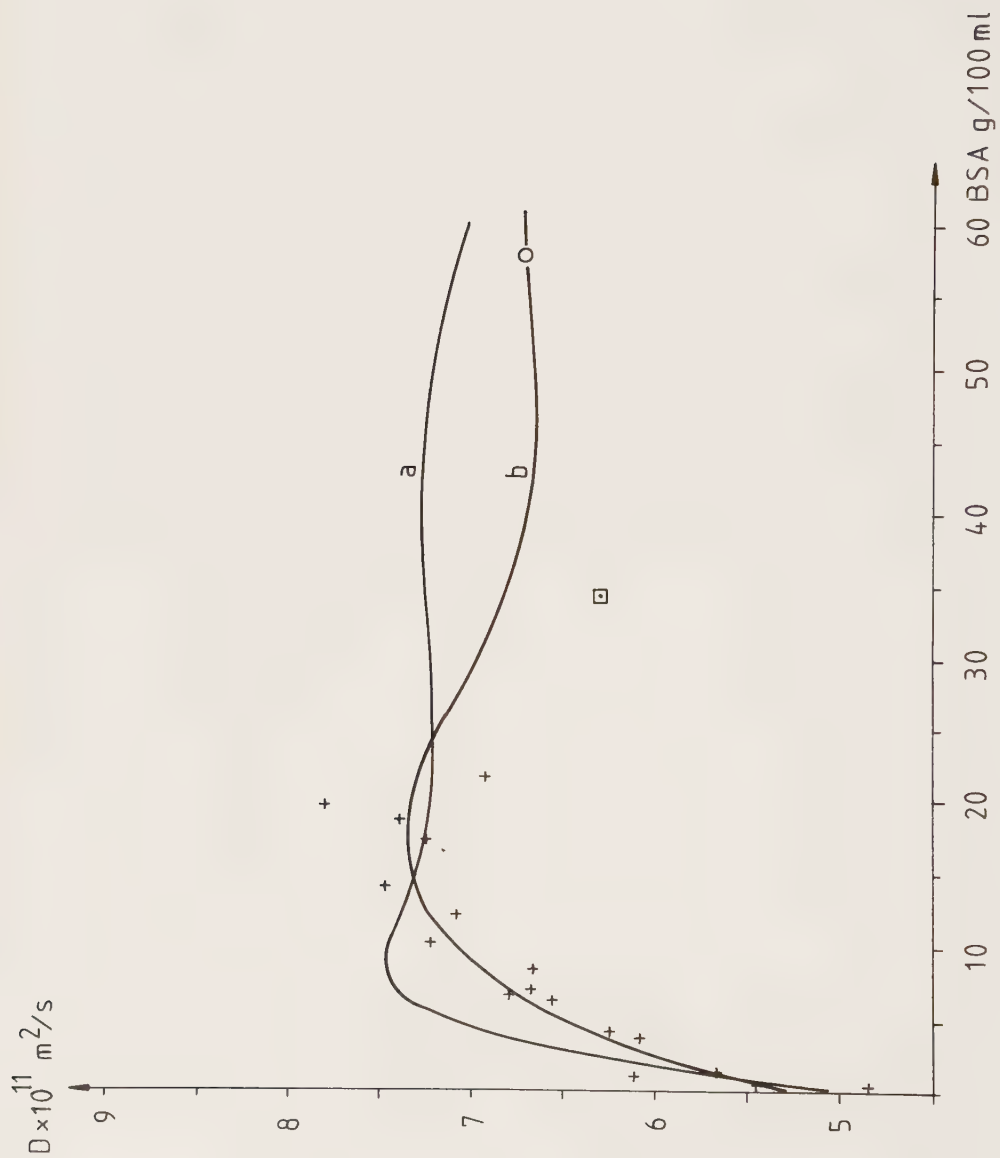


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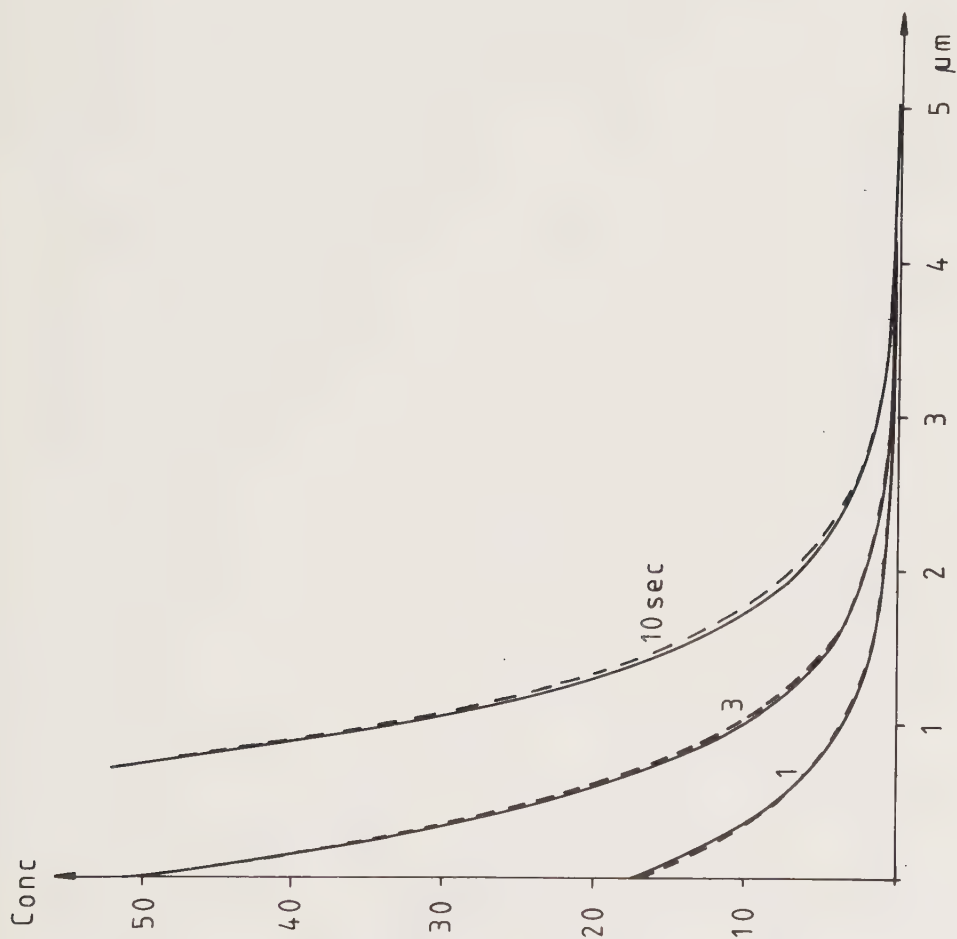


Fig. 4.

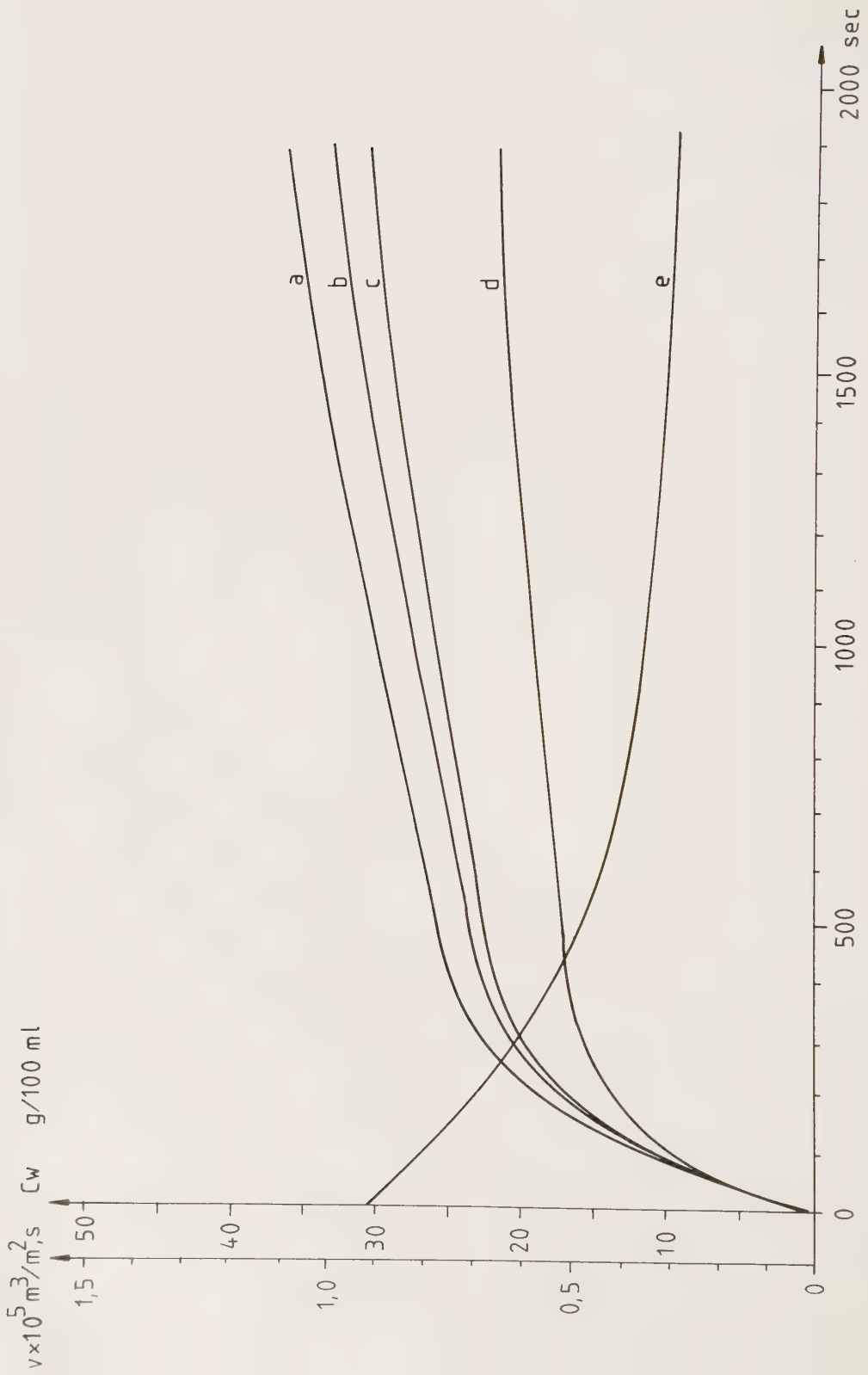


Fig. 5.

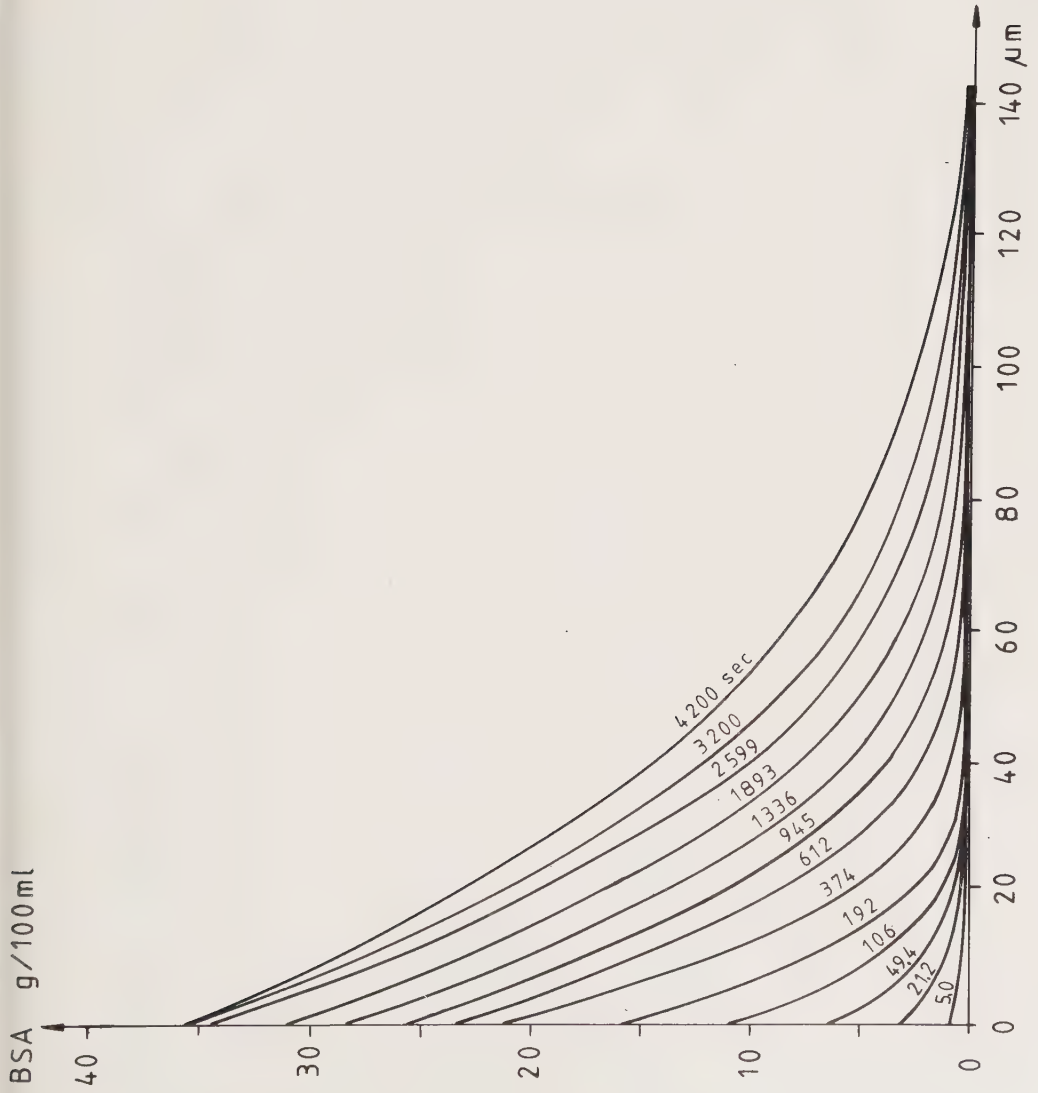


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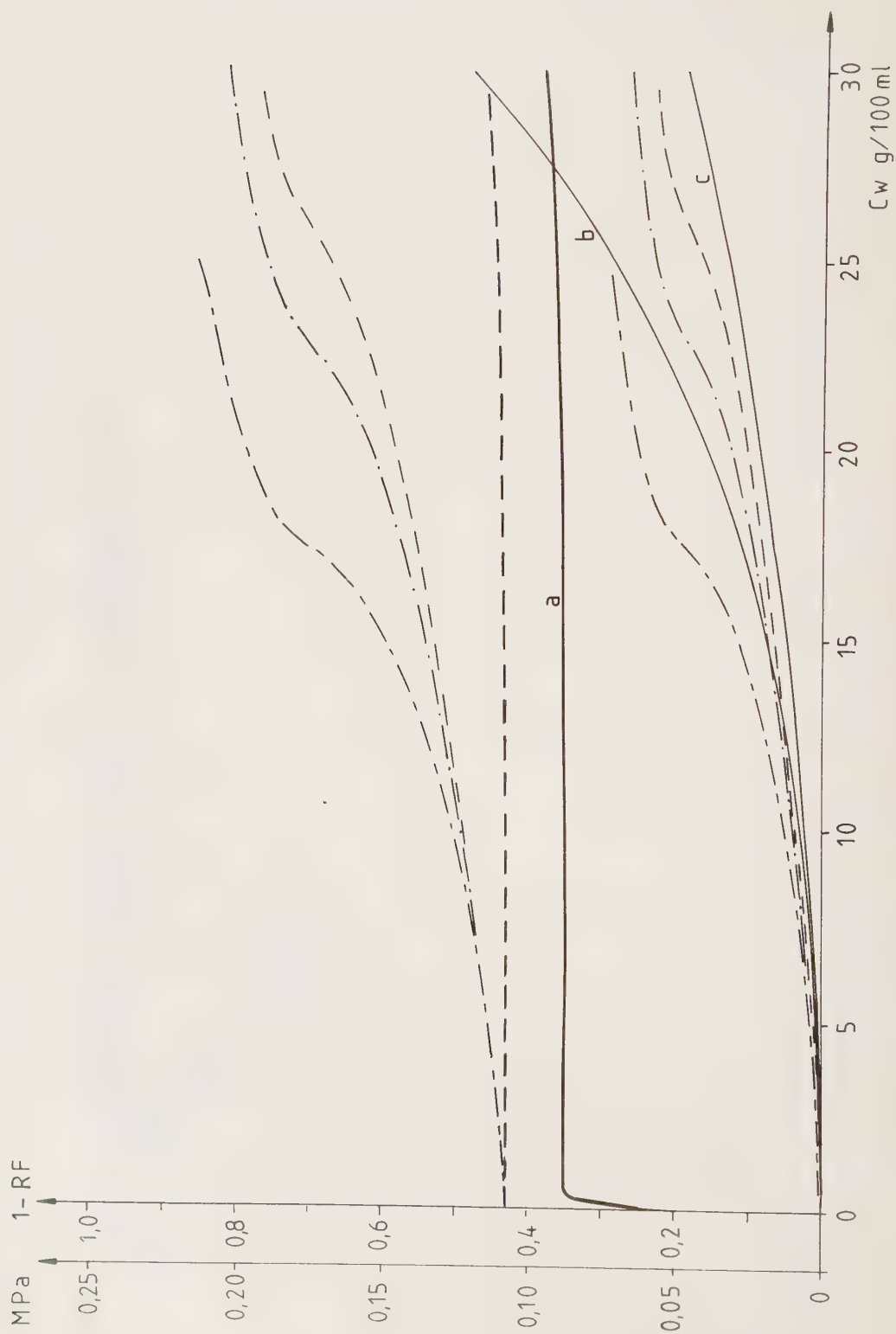


Fig. 7.

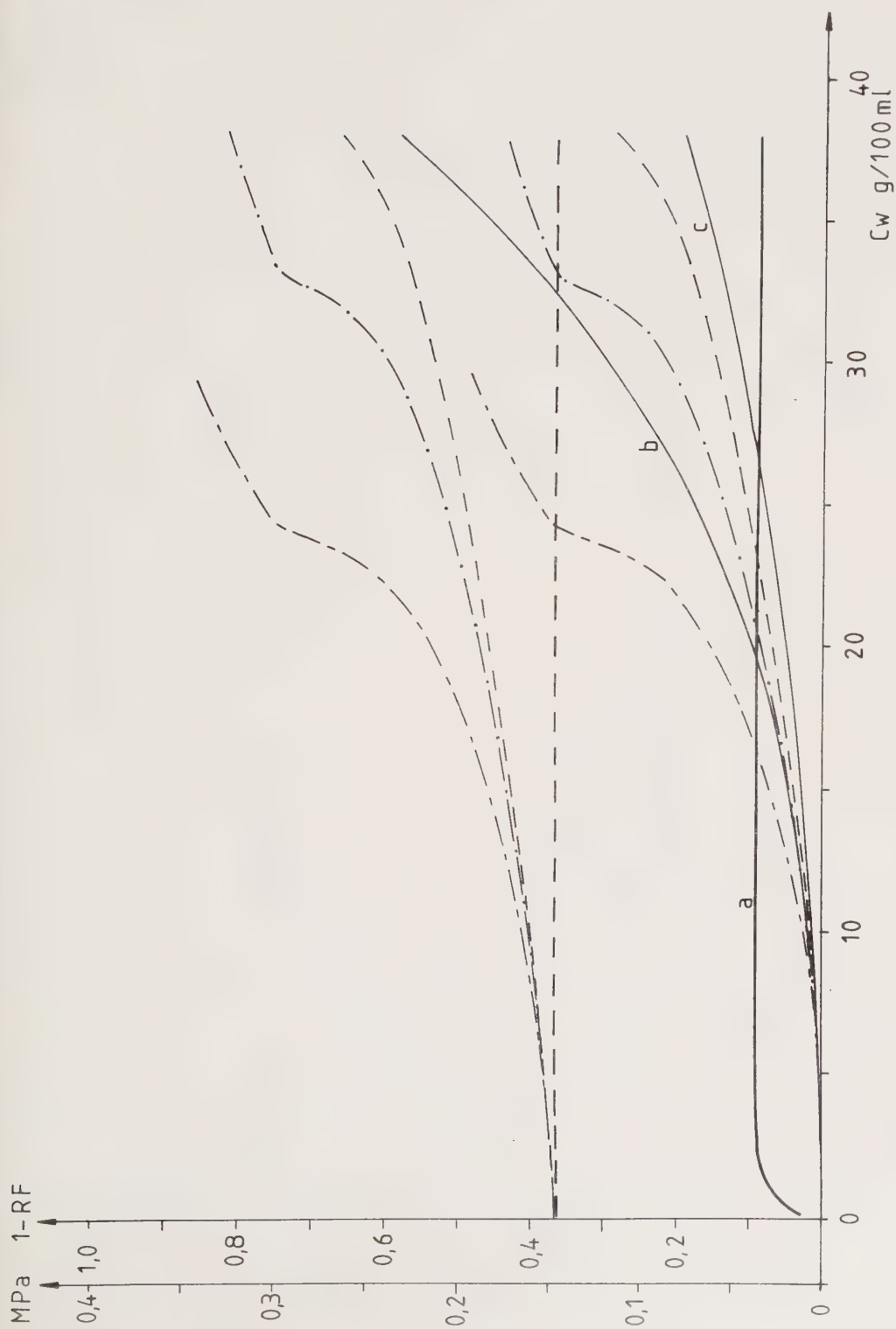


Fig. 8.

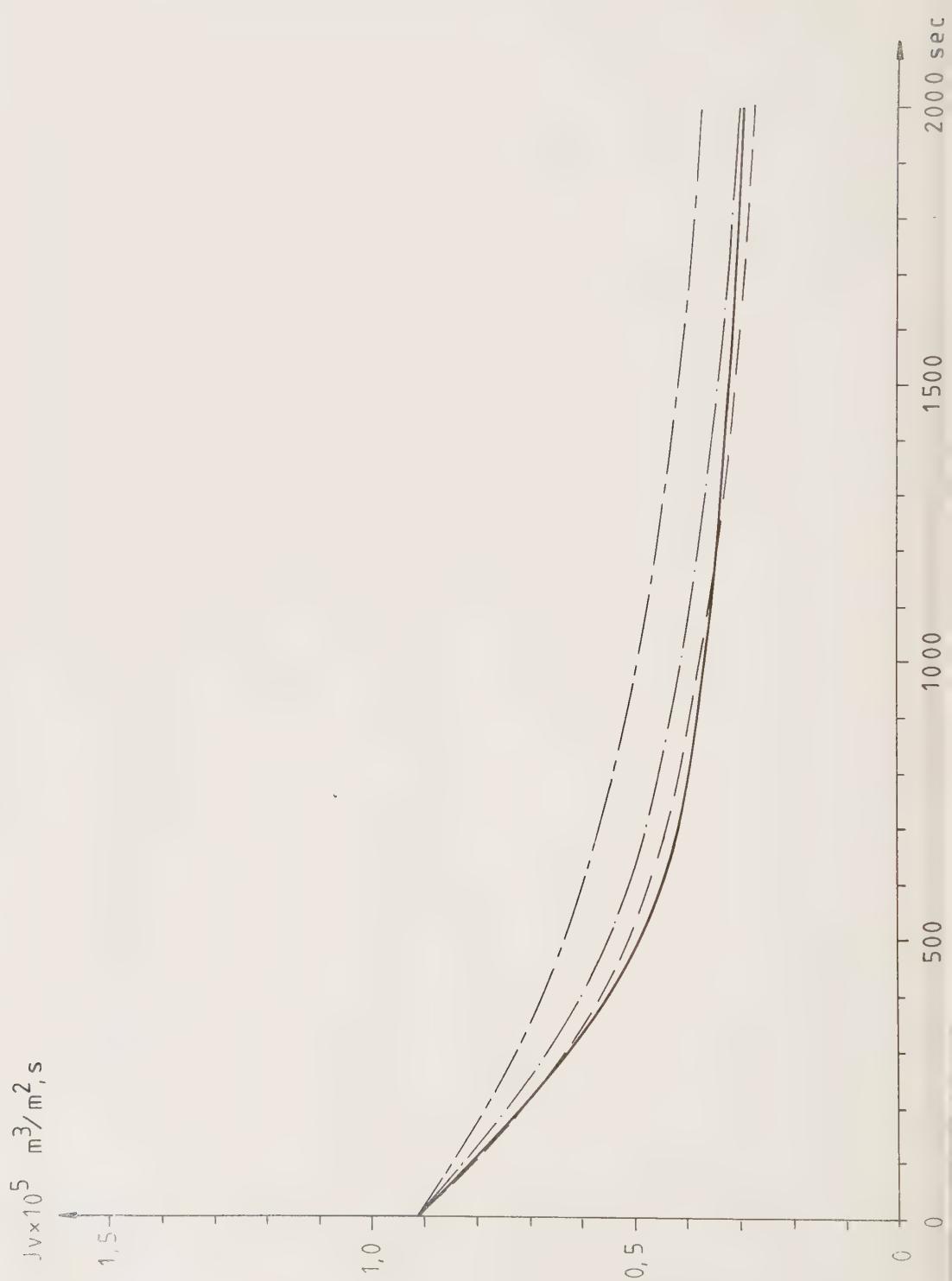


Fig. 9.

